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**CHARACTERIZATION OF LIQUID FUELS BY FLASH PYROLYSIS OF COAL
IN VARIOUS ATMOSPHERES**

City University of New York

Ph.D. 1984

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CHARACTERIZATION OF LIQUID FUELS BY FLASH PYROLYSIS
OF COAL IN VARIOUS ATMOSPHERES

by

Shi-Jin Shen

A dissertation submitted to the Graduate Faculty
in Engineering in partial fulfillment of the
requirements for the degree of Doctor of Philosophy,
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ABSTRACT

An evaluation of the quality and yields of liquid fuels obtained by flash pyrolysis of coal is the objective of the present research. The flash hydrogenation of a Pittsburgh No.8 coal in a laboratory reactor has been examined as a part of this research. The yield results are interpreted and compared with those presented previously for flash hydrogenation of another bituminous coal - Illinois No. 6 coal. A simple reaction model is proposed to explain the behaviour of both coals under flash hydrogenation.

Liquids obtained by flash hydrogenation during pilot plant runs are compared with steam pyrolysis liquids obtained in the same unit. Each liquid sample was fractionated by a modified SESC (Sequential Elution with Selective Solvents Chromatography) method. Each fraction was then analyzed by simulated GC (gas chromatography) boiling point distribution curve method, steric exclusion chromatography, and ^1H NMR. The liquid products from hydropyrolysis are comparable to those from H-coal and Synthoil processes. The steam/helium pyrolysis liquids are rather different from those obtained by hydropyrolysis.

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Chapter I

INTRODUCTION

Since the energy crisis, people become aware that the crude oil resources are limited. There has been substantial interest in finding alternative energy resources. Coal, due to its high relative abundance, wide geographical distribution and ease of conversion of the techniques and equipment from those used for gas and/or oil, has once more become the focus of energy research.

Many research and development projects have been started, with the objective of establishing technically reliable and economically feasible coal conversion processes to better synthesize liquid fuels. Coals are complex heterogenous mixtures, which have marked diversity under various reactions. Therefore, an understanding of coal properties and their influence in conversion processes is extremely important. The following section is an introduction to coal liquefaction processes.

1.1 COAL LIQUEFACTION PROCESSES

Flores (1982) classified four major types of processes for converting coal to liquids: pyrolysis, solvent extraction, catalytic liquefaction, and indirect liquefaction.

In solvent extraction processes, coal is mixed with a solvent which can transfer its loosely bound hydrogen atoms to the coal. Heating not only overcomes many of the physical interactions in the coal such as Van der Waals forces and hydrogen bonding forces but also breaks weak chemical bonds. The solvent then promotes hydrogen transfer to the broken bonds. The recycle solvent, usually a mid-distillate of process-derived liquids, is continuously recovered and recycled to the extraction vessel. The ash in the extraction vessel can act as a catalyst for the solvation process. The solvent extraction processes include: Solvent-Refined Coal (SRC), Consol Synthetic Fuel (CSF), Co-Steam, and Exxon Donor Solvents (EDS).

Catalytic liquefactions are those hydrogenation processes in which catalysts other than the mineral matter naturally occurring in ash are used to promote hydrogenation of the hydrogen donor solvent. The catalysts usually used are FeO, MoO, ZnCl_2 , NiCl_2 or some commercial catalysts such as Co-Mo and Ni-Mo. These processes have the advantage that a separate reactor to rehydrogenate the solvent is not

required. However, catalyst deactivation and separation problems have been encountered. Two types of solutions are employed; the first type, the catalyst and the coal are in direct contact in the reactor, hydrogen gas is introduced, and rapid hydrogenation is achieved. The liquid-phase ZincChloride and the experiments of Schroeder are examples of this processes. In the second type, the coal and the catalyst are not in direct contact, but the suspended pelletized catalyst promotes hydrogenation of the carrier solvent, which in turn hydrogenates the coal. Examples include H-coal, Synthoil, and Gulf Catalytic Coal Liquefaction.

Indirect liquefaction is the gasification of coal to produce synthesis gas ($H_2 + CO$) followed by water-gas shift and catalytic conversion to produce liquid hydrocarbons and oxygenated compounds. Indirect liquefaction processes include Fischer-Tropsch, methanol synthesis, and Methanol to gasoline.

Pyrolysis, or devolatization, is defined as the heating of coal in the absence of air or oxygen in order to obtain gases, light liquids, heavy oil and char. When pyrolysis is carried out in the presence of hydrogen it is called hydropyrolysis. Pyrolytic processes typically convert about forty percent of the coal to char. Thus, these processes appear to be best suited to plants that gasify char to

produce synthesis gas, hydrogen, or fuel gas. When hydrolysis is carried out with high reaction temperatures, high heating rate and controlled vapor phase residence time, it is called flash hydrogenation. In flash hydrogenation, the products devolatilized by hydrolysis of coal are upgraded by contact with hydrogen for a controlled residence time. Using very short residence times at high pressures in the presence of hydrogen improves liquid yields but may require additional processing to upgrade the products obtained. Pyrolytic processes include Lurgi-Ruhrgas, Char Oil Energy Development (COED), U.S. Steel Clean Coke, and Coalcon. Present research focuses on the liquid products from flash pyrolysis in various gas atmospheres.

1.2 FLASH HYDROGENATION

The products of hydrolysis of coal are gases, liquids and solids. The parameters which may affect the nature and the characteristics of the products of hydrogenation are: the method of hydrogenation - the reactor, type of coal, reaction temperature, reaction pressure, hydrogen partial pressure, coal particle diameter, pretreatment of coal, residence time of gas, residence time of solid, heating rate of coal, ratio of hydrogen to coal, and catalyst(Anthony and Howard, 1976). These parameters will be considered in detail in the next section.

It is difficult, however, to individualize the effect of each processing variable with assurance due to the fact that the changing of one variable will affect the other. For example, when the reaction temperature and pressure are changed, the vapor residence time is also changed; if the vapor residence time has to be kept as a constant, then the gas flow rate has to be changed thereby causing the ratio of hydrogen to coal to change. Or when the particle diameter of coal is changed, the heating rate will be changed too. There is difficulty in isolating the effect of each processing variable.

In studies previously reported by this laboratory (Clean Fuels Institute of CCNY) on flash hydrogenation (Graff et al. 1976, Dobner et al. 1976), there have been references to the production of components that were beyond the analytical capability of the experimental equipment in use. The analysis of products from flash hydrogenation of coal was performed by mass spectrometry, but the instrument is limited (when online with the reactor system) to components with the molecular weight of xylene or lighter. If compounds of molecular weight higher than xylene are produced, they are not detected. The liquid product yield was calculated then from the converted carbon mass balance.

Although these previous studies made good progress toward explaining flash hydrogenation behavior, it is clear that

the heavier liquid fraction is an important part of flash hydrogenation of coal. The knowledge of the constitution of coal derived liquid could throw light on the chemical mechanisms of the reactions that occur during coal flash hydrogenation. Moreover, the liquid product is valuable because it can be used directly as a petrochemical feedstock or can be processed into more valuable products. In an industrial refining application, three problems are associated with the upgrading of coal liquids into useful transportation fuels. The first is attributed to their inherent instability, i.e., the tendency of these materials to polymerize, which is a trait linked to comparatively high heteroatom content in coal derived liquids. The second problem is that the removal of these heteroatoms calls for high pressure and temperature treatment with concomitant consumption of hydrogen. Catalyst poisoning is the third problem. The higher the heteroatom content, the higher will be the consumption of hydrogen and greater the tendency to poison the catalysts.

1.3 PURPOSE OF THIS RESEARCH

For the above reasons, this research was set up with the aim of proposing a methodology to evaluate the coal liquid product and obtaining more information on the properties of the liquid fraction from coal hydropyrolysis and steam pyrolysis. At the beginning of this research, there were

few publications concerned with characterization of coal derived liquids, and no studies were available on liquid products from flash pyrolysis or flash hydrogenation. Only in the past two years (1982 and 1983), have papers dealing with separation and characterization of coal derived liquids from different coal processes appeared in literature. To accomplish these objectives, several analytical techniques have been juxtaposed to improve the understanding of coal derived liquids. The elemental composition gives the average heteroatom content of the liquid sample plus some information on the quality of the fuel. Steric exclusion high pressure liquid chromatography gives the molecular weight distribution of the sample as well as its average molecular weight. Simulated boiling point distribution curves obtained by a gas chromatographic method give average boiling points and the percentage of light oil and resid. Hydrogen NMR spectroscopy gives the ratio of aliphatic to aromatic hydrogen.

If the above analyses are performed on an entire liquid sample, the informations obtained are only on an "average" hypothetical molecule or model compound of the coal derived liquid. The truth is, however, that the coal liquid is composed of a wide range of molecular species of different sizes, functionalities, and heteroatom contents. It is of interest to establish how the heteroatom functional groups, molecular sizes and aromaticity are distributed. In order

to obtain such distribution, it is necessary to fractionate or separate the components of the liquid. Since a component by component separation and identification would be an impractical task, it is usually preferred to fractionate the coal derived liquids into families of components having common physical or chemical properties. The SESC (Sequential Elution with Selective Solvents chromatography) is a separation technique based upon polarity and functionality. The purpose of SESC was to use a series of elution solvents which would separate specific classes of components from Solvent Refined Coal by polarity and functionality. This technique was adopted with minor modification to separate liquid products obtained from coal flash pyrolysis. Each fraction then characterized by steric exclusion chromatography for molecular weight, simulated boiling point GC method to get boiling point distribution, elemental analysis for elemental composition, and hydrogen NMR spectroscopy for aromaticity. Hence the knowledge of the nature and structure of the coal liquid products from flash pyrolysis can be improved.

Since the amount of the coal liquids produced under steam pyrolysis in our laboratory was too scant for more detailed analysis, Cities Service R&D Co. provided coal liquids from runs WKB-68 and WKB-77 from its pilot plant to us. In the Cities Service R&D plant, coal was treated under identical reaction conditions. One sample was reacted under hydrogen,

and the other under steam/helium atmosphere to allow a comparison of gas and liquid yields (details in sec. 3.4).

The yield trends of pyrolysis of coal in different gaseous environments have been explored by many investigators. Investigations of the effects of steam and hydrogen on pyrolysis of hydrocarbons, coal and vacuum residuum (Szuba and Michalik 1982) indicate that both steam and hydrogen influence the yield. Recently, Szuba and Michalik (1982), have shown that the total production of liquids from pyrolysis is higher in the presence of steam than in an inert atmosphere, but is still lower than in hydropyrolysis. In this study, this trend has been confirmed. In addition, coal liquid products were subjected to fractionation by modified sequential elution with selective solvents chromatography (SESC)(Farcasiu 1977), followed by molecular size determination using steric exclusion high performance liquid chromatography (HPLC), simulated boiling point distribution by GC and H-NMR spectroscopy in order to have an overall view of coal derived liquids.

Chapter II

LITERATURE REVIEW

2.1 LITERATURE REVIEW ON PYROLYSIS AND HYDROLYSIS

2.1.1 Previous Reviews

Lowry (1945, 1963) compiled reviews which covered the chemical aspects of coal pyrolysis reaction and coal gasification technology. Jones (1964) reviewed several low-heating rate pyrolysis publications and Yellow (1965) critically evaluated a number of low heating rate studies. Badzioch (1967) commented on high heating rate pyrolysis studies. Essenhigh and Howard (1971) examined combustion and explosion phenomena in coal dusts in the pyrolysis literature. Pyrcioch et. al. (1972) reviewed the vast coal gasification research done at the Institute of Gas Technology. Coal devolatilization and hydrogasification researches were critically evaluated by Anthony and Howard (1976), and an in depth review of kinetic models was presented. Suuberg (1977) examined the effects of experimental parameters on rapid pyrolysis and hydrolysis. A review of process concepts for flash hydrolysis was presented by Greene et. al. (1980). Elliott (1981) composed review articles in which Howard

(1981) critically reviewed coal pyrolysis and hydropyrolysis, Essenhigh (1981) commented on coal combustion, J. L. Johnson (1981) examined coal Gasification and Gorin (1981) reviewed coal liquefaction. McNeil (1981) in that work examined the properties, analyses, and processing of high-temperature coal tar. Chen (1981) tabulated the experimental techniques and conditions on devolatilization and hydrogenation researches during the last few years, and also commented on the effect of operation variables in the process. Furfari (1982) reviewed critically the process of hydropyrolysis of coal. Gavalas (1982) also reviewed recent results of pyrolysis research.

Further experimental results on pyrolysis were published by Juntgen and Van Heek (1979, 1981), Suuberg et al. (1980), Franklin et al. (1981), Fynes et al. (1981), Mackie and Doolan (1981), Scaroni et al. (1981), Soloman et al. (1981), Suzuki et al. (1982), Hauge et al. (1983), Tyler and Schafrer (1980), Desypris et al. (1982), Schaub et al. (1981), Cypress and Furfari (1982), and Wilson et al. (1982) did investigation on flash pyrolysis or hydrogenation on coal. Stangeby and Sears (1981), Eklund and Wanzl (1981), McCown et al. (1982), and Niksa et al. (1982) studied pyrolysis and hydropyrolysis of coal. Most of the above investigators used rapid heating (more than 100 C per second) rate in their experiments. Cypress and Furfari (1982), Wilson et al. (1982), Derbyshire et al. (1981),

Franklin et al. (1982), and Kuhn and Plogmann (1983) did research on mineral matter effects on pyrolysis or hydrolypyrolysis.

2.1.2 Liquid Analysis

In spite of the considerable amount of research on the structure of coal that has been reported in recent years there is still a lack of fundamental knowledge and a certain amount of controversy. This is partly due to the heterogeneity of coal, its insolubility in most solvents, and variations among coals. The inherent properties of coal restrict the techniques that can be usefully applied to structural characterization. Because of the complexity of coal derived liquids, determination of the actual compounds present is generally impracticable at present. Elemental analyses may be made (White and Whittingham 1983), giving the content of carbon, hydrogen, nitrogen, sulfur and oxygen. Viscosity of coal derived liquids can be obtained (Baltatu 1981). However, such analyses give little indication of the actual character of coal derived liquid. The complexity of many organic mixtures of coal and coal derived liquids makes it necessary to separate the liquid into a number of fractions based on chemical or physical properties. The ability to separate coal-derived liquid products into meaningful fractions and to identify the key chemical features of these fractions is needed to develop an

understanding of the mechanisms involved in coal liquefaction and to discover improved processes.

It is always easier to characterize distillable materials than non-distillables. Distillable materials can always be characterized by distillation (Dooley and Thompson 1977, Schweighardt et al. 1981, Liphard 1981, Collin et al. 1983, Hasen et al. 1983). The boiling point distribution can be measured directly, or a simulated boiling point distribution curve can be obtained by a gas chromatography (GC) method (ASTM D2887-1973). Stompel et al. (1982) investigated low molecular weight aliphatic and aromatic components of coal derived liquid by glass-capillary GC. Schweighardt et al. (1981) used GC to analyze coal derived liquid. Burchill et al. (1983) employed GC with a nitrogen-selective alkali-flame detector and mass spectrometer to identify nitrogen compounds in coal tar. Although major peaks of GC can be identified, GC has limitations when characterizing coal derived liquid in that several components can elute at the same time. Moreover different chemical classes components have diverse response factors even with flame ionization detection. Actually Schweighardt et al. (1981) found that under GC coal derived liquids do not respond (retention time vs. response factor) linearly with flame ionization detector (FID) but do respond linearly with a thermal conductivity detector (TCD). Burchill et al. (1983) also reported some interferences from hydrocarbon

with their nitrogen-selective alkali-flame detector. Thereby making quantitation or even quantitation by GC methods is rather difficult. Furthermore the molecular weight range amenable to the GC methods is more restricted (approximately to 300 M/Z) than that accessible to liquid Chromatography (LC) methods.

The traditional method uses solubility in organic solvents to separate oils, tars, etc.. Solvent fractionation of coal liquids and petroleum products has long been an important method for characterization, and several standard methods exist. For example, Brucke (1979) found that asphalts, pitches and many heavy petroleum products are characterized by trichloroethylene solubility and insolubility in benzene, dimethylformamide, quinoline, pentane or heptane. Coal liquids, being more complex than petroleum, have been fractionated in the above solvents and also in chloroform, carbon disulphide, tetrahydrofuran(THF), and pyridine. Solvent extraction has been widely used to separate the coal derived liquids into hexane-soluble (oils) or pentane-soluble (maltenes), pentane or hexane insoluble but benzene-soluble (asphaltenes) and benzene insoluble but pyridine-soluble (pre-asphaltenes) by Mima et al. 1978, Schweighardt et al. 1981, Stempel et al. 1982, also Stempel and Bartle 1983. Although such separations are popular, Schultz and Mima (1978) pointed out that different procedures for the same material can give significantly different results.

In addition, the solubility of a compound is not solely dependent upon its own structure and functionality but also that of other surrounding compounds. Hence, a given component can appear in one fraction or another depending upon the absence or presence of other substances in coal liquids. Therefore, separation by adsorption chromatography on silica or alumina have been used. For example, Wollarb et. al. (1963) and Bartle (1978) used silica gel column chromatography, Watkins (1967) and Snyder (1968) used preheated silica gel with improved efficiency to obtain the separation of coal liquids in different classes. Treatment with concentrated sulphuric acid by Ahmad et. al. (1966) or iodine monochloride by Jurriens (1965) and by Spence et. al. (1967) prior to silica gel chromatography was used to separate olefins from light petroleum fractions. Farcasiu (1977) first separated solvent refined coal (SRC) liquids in terms of fractions of different chemical functionality by sequential elution chromatography with specific solvents (SESC) on silica gel columns. The solvents used were hexane, hexane/15% benzene, chloroform, chloroform/10% ether, ether/3% ethanol, methanol, chloroform/3% ethanol, THF, pyridine, and pyridine/10% methanol/20% water. SESC was used by Dark (1978) to separate asphalts, by Weiss (1980) and Hausler et al. (1981) to separate coal liquefaction products for trace element characterization, by Bennett and Fredericks (1982) to separate SRC liquid, also

by Jacobs and Filby (1983) to separate asphaltenes extracted fraction from oil sands and crude oils.

Complicated coal derived liquid or its fractions can also be separated into acid, neutral and basic fractions by extraction with acid and base (Dooley and Thompson 1977, Liphard 1981), or by chromatograph on ion-exchange resins (Odoerfer et al. 1981, Young et al. 1983, also Koplick and Wails 1983). Usually the basic fraction has high nitrogen content due to pyridine groups, while the acidic fraction has high oxygen content due to phenolic groups.

Gel permeation chromatography (GPC) or steric exclusion chromatography (SEC) was used to separate aliphatic and aromatic hydrocarbons according to their molecular size and shape by Hendrickson et. al. (1966), Hsich et. al. (1969), and Yokoyama et. al. (1979). Separation of aliphatic hydrocarbons from a mixture of coal liquids by molecular sieves was achieved by Eiglington et. al. (1964). Coleman et al. (1976, 1977) used GPC with three different packing materials to separate SRC fractions. Dooley and Thompson (1977), Schanne and Haenel (1981), and Ignasiak et al. (1983) fractionated coal derived liquid or asphaltene by different molecular weight ranges with GPC techniques. Schwager et al. (1979) and Curtis et al. (1980) studied SRC liquids using GPC methods. Yoshii and Sato (1979) used GPC to fractionate hexane-soluble portion of the pyridine

extract from coal. Philip and Anthony (1982) separated coal derived liquid into aromatic, phenolic and asphaltenic fraction by GPC methods. Khan (1982) compared the use of GPC and Vapor Pressure Osmometry (VPO) to get molecular weight data for hexane-soluble fraction of three H-coal liquids.

To determine the molecular weight of fractions obtained by GPC the difficulty of finding suitable standards for column calibration has to be overcome. And in spite of no interaction between the packing materials of GPC and coal derived liquid was reported in literature, interactions between the gel matrix (Sephadex G types) and the nitrohumic acids while separation of humic acids by GPC were found (Moliner et al. 1982). Those interactions were two types: one has non-polar character and operated through the electrons of the aromatics; the other has polar character and acts by means of functional groups such as -OH, -NH₂ and -COOH, bonded to the aromatic rings. From the nature of these interactions, the possibility of having interactions between the gel matrix and coal derived liquid is not excluded. Hence the results obtained from GPC separation has to be interpreted with caution.

The other common way using LC to characterize coal derived liquid is to separate the sample into saturates, aromatics and polar fractions (Ekinçi et al. 1982, Stompel

et al. 1982). Young et al. (1983) used silica gel column divided upgraded coal derived liquid into saturates, aromatic I and II fractions. Dark and McFadden (1978) used an amino column with a non-polar solvent with backflushing to obtain the polar components. Fredericks (1981) separated the non-polar material of the processing solvent from an SRC process using a silica gel column and a non-polar mobile phase into saturates, one-ring aromatics, two-ring aromatics, other aromatics and slightly polar material. Yokoyama et al. (1981) split hexane-soluble oil into saturates, aromatics, polyaromatic polar groups by LC and also separated that oil into saturates, mono-aromatics, diaromatics, tri-, tetra-aromatics and polyaromatic polar fractions by modified USBM-API method.

Mass spectrometry (MS) provides information about molecular structure usually by using relatively pure compounds and sufficient ionization energy to cause chemical bonds of the molecule and fragment be ionized. In general the spectrum of ion intensity vs. mass is highly characteristic of the molecule. For complex mixtures or samples that are not sufficiently volatile or thermally stable for vaporization and separation, MS cannot give useful structural information. Hill et al. (1981) used MS and MS-MS to characterized coal derived liquid from Exxon Donor Solvent process. Ciupek et al. (1983) used MS-MS to analyzed SRC-II liquids. They admitted that the comparison

between spectra of components of mixtures and those of standard compounds is difficult, even with mass spectral libraries. Moreover the MS spectra are very dependent on the nominal collision energy and pressure. Besides it is possible for more than one component contributed to a particular ion in a complex mixture. The use of MS alone in coal derived liquid characterization is not promising.

In another approach, since the identification and quantitative separation of all the components of a complex coal derived liquid is impracticable, the chemical composition of coal derived liquid can be obtained in terms of the 'average' structural parameters obtained by spectroscopic methods. Infra-red (IR) spectroscopy was used by Brown (1955) to study the aromaticity of coals and coal products. Information about a number of important functional groups, such as aliphatic , aromatic, hydroxyl, and carbonyl, from their absorption in the infra-red region of the electromagnetic spectrum can be obtained by IR spectroscopy. Good quality spectra of poorly transmitting materials such as coals, coal derived liquids etc., are difficult to obtain from conventional IR spectrometers because of the poor energy throughput with the grating and slit optical systems. Koenig (1975) used an interferometer instead of a monochromator to obtain interferograms which then subjected to a computerized mathematical process - Fourier Transfromation to yield the IR spectrum. Fourier

transfrom infra-red (FTIR) spectrometers have much improved sensitivity and accuracy, moreover the results can be manipulated much easier. Solomon (1978, 1979, 1981, 1982) used FTIR to determine the aliphatic CH, aromatic CH, the oxygen functionality and mineral contents of coals and coal products.

Williams (1958) used hydrogen nuclear magnetic resonance (^1H NMR) to characterize hydrocarbons in petroleum oils. Coleman et al. (1976) and Wooten et al. (1976,1978) analyzed hydrocarbons by ^1H NMR. Collin et al. (1980) also Stompel and Bartle (1983) used ^1H -NMR to study flash pyrolysis tar and found the hydrogen distributions, the aromaticity, the degree of substitution of aromatic rings and the atomic hydrogen to carbon ratio. Lynch and Webster (1981) used ^1H NMR for the dynamic study of the thermaplasticity in coal. Shooley and Budde (1976), Takegami et al.(1980) and Gillet et al. (1981) reported the use of Carbon NMR for the analysis of hydrocarbon types in crude oils and crude oil products. Friedel (1959) , Brown and Ladner (1960), Rectrofsky and Friedel (1970), Bartle et al. (1975), Yokoyama et al. (1979), Clarke et al. (1982), and Hasan et al. (1983) used both ^1H as well as ^{13}C NMR spectroscopy for the analysis of coal derived liquids.

NMR spectroscopy can measure the signal from a particular nucleus which is dependent on its magnetic environment and

is a function of the molecular structure. The aromaticity obtained by NMR is the proportion of the hydrogen or carbon that occur in aromatic ring structures. In addition by dividing the spectrum into different regions and attributing the signals in each region to different hydrogen or carbon types based on experiments with model compounds, more information can be obtained. Cookson et al. (1981) obtained separate NMR spectra for the quaternary, methine, methylene and methyl carbons. Joseph et. al. (1980) used ^{13}C Carbon Fourier Transform Nuclear Magnetic Resonance (^{13}C -FTNMR) to get the aromaticity, the ratio of aromatic to aliphatic carbon, the absolute number of carbon atoms per molecule base, the distribution of carbon and the average molecular structure of H-coal liquids.

The use of NMR spectroscopy can be recorded in relatively short times, providing detailed compositional characteristics which other methods can not offer. However, generally solid materials have to be analyzed in solution such as deuteriochloroform or deuteropyridine. This means that the information can be obtained only for materials soluble in chloroform or pyridine. Zilm et al. (1979) employed a solid state NMR and avoided the above disadvantage. Hydrogen NMR is much simpler to perform but yields less information due to the fact that the narrow range of chemical shifts which results in broad unresolved signals. And also because the hydrogen structure can not

five as much useful information about the chemical structure as the carbon skeletons. Carbon NMR spectrometer can give direct information on the carbon structure over a wide range of chemical shifts with better resolution. Hasan et al. (1983) pointed out that there are two inherent problems in obtaining quantitative results by ^{13}C NMR. First, quaternary carbons have longer spin-lattice relaxation time than other types of carbon since in an FTNMR experiment all nuclei must be fully relaxed and returned to their equilibrium state before a repetitive pulse can be applied, and a few thousand pulses are needed for one spectrum several days may be necessary for one measurement. By using reagents which can help relax the carbon nuclei, the above problem can be minimized. The other problem, unequal nuclear Overhauser enhancement of different types of carbon nuclei, can be eliminated by setting the spectrometer in the gated decoupling mode.

Fluorescence spectroscopy has been used for identification of various polycyclic aromatic hydrocarbons and their heterocyclic analogues by Popl et al. (1974), Kershaw (1978), Curtis et al. (1980), and Katoh et al. (1980). Kershaw (1983) tried to use fluorescence spectroscopy for the identification of nitrogen bases and certain aromatic ring systems in coal hydrogenation liquids. Unfortunately there are only few model compounds reported spectra available and the sample has to be analyzed under

the same condition as the model compound for comparable results.

Since GC and LC are primarily separation tool, they are best combined with a characterization technique to identify individual components. For example Dark et al. (1977) used LC-MS, Hubball et al. (1980) used GC-IR, and Brown et al. (1980) used LC-IR to analyze coal derived liquids. The most used technique is GC-MS. In this technique the effluent from the GC column is led into the ionization chamber of a MS, either directly or after passing through an interface to remove some of the carrier gas. The MS continuously scans and the data is collected and compared with spectra library in a computerized data system. Ideally, each peak from the GC consists of only one component and produces a sufficient number of scans for a quality spectrum of that component to be obtained. Mass spectrometry combined with GC was used efficiently by Bartle et. al. (1979) in identifying numerous components of coal tar.

However, no single analytical method can provide all of the information necessary to advance the understanding in this developing technology. A combination of two or more analytical techniques to study coal liquids are increasingly used by investigators lately. Aliphatic and aromatic hydrocarbons were separated by gas chromatography and analysed by ^1H -NMR by Coleman et. al. (1976), and Wooten

et. al. (1976, 1978); or further separated by GPC and analysed by ^1H -NMR and ^{13}C -NMR by Yokoyama et. al. (1979). Gavallas and Oka (1978) fractionated vacuum pyrolysis tar by GPC into three molecular weight range fractions. Each fraction was analyzed by hydrogen NMR and elemental analysis. Shadle et. al. (1982) also used ^1H -NMR and GC-MS to obtain structure features in the coals and the asphaltenes derived from them. Stompel et al. (1982) solvent-fractionated rapid pyrolysis tars into oils, asphaltenes and preasphaltenes. The first two fractions were separated further by LC. Oberg et al. (1982) used distillation to separate the liquid product from flash hydropyrolysis pilot plant into three fractions. The first two fractions were analyzed to define density, nitrogen and sulfur content, calorific values, percentage of insoluble and ash contents. They also fractionated the liquid products into oil, asphaltene, preasphaltene, and unreacted coal. Farcasiu (1977) separated SRC liquids into ten different fractions by SESC techniques. Each fraction then underwent various analytical methods such as VPO, GC, ^1H -NMR, and ^{13}C -NMR to get more information on its structure. Painter et. al. (1979) used FTIR for SESC fractions of an SRC liquid to identify various types of hydrocarbons and the functional groups. Schwagner and Yen (1977) divided coal derived liquids by LC with benzene, pentane, propane, and carbon disulfide as solvents, then

characterized the fractions by elemental analyses, molecular weight and color intensity determination, NMR, IR, and X-ray diffraction analyses. Dooley and Thompson (1977) separated coal liquids from COED and Synthoil liquefaction processes using distillation, gradient elution LC, acid and base extractions and GPC, then each fraction was analyzed by MS and NMR. Yen et. al. (1979) used solvent fractionation to isolate asphaltene and preasphaltene fractions, further separated by LC or GPC, then characterized by various chemical and physical methods: elemental analyses, x-ray diffraction, ^1H -NMR, ^{13}C -NMR, IR, polarography, thermogravimetric analysis, electron spin resonance (ESR), U.V. spectroscopy, MS, transmittance electron microscopy, oxidation, self-association, and densimetric methods.

Barkle et. al. (1979) also used sequential elution of coal liquid and petroleum products injected onto an glass beads column by using (1) hexane, pentane (2) toluene, benzene and (3) pyridine and THF respectively. Schwager et. al. (1979) applied liquid chromatographic separation (solvents used were benzene, ethanol and THF) on silica gel columns for coal-derived asphaltenes to get three different fractions. Hereupon, molecular weight and NMR methods have been used to deduce features of the microstructures of those fractions, chemical and instrumental method were used to determine qualitatively and quantitatively the composition of the functional groups -OH, -NH, and -N. Further, the

macrostructure of asphaltene crystallites was studied by x-ray diffraction methods while the nature of the association between asphaltene molecules was studied by electron spin resonance. Curtis et. al. (1980) used GPC to separate a SRC liquid into six fractions, verified by chemical ionization and electron impact mass spectrometry. Each fraction was further analyzed by infrared spectroscopy (IR), elemental analysis, fluorescence excitation and emission spectrometry, HPLC and GC. Liphard (1981) used distillation then acid and base extractions to divide distillate oil from KOHLEOEL coal process. Stompel et al. (1983) employed solvent extraction separating rapid pyrolysis tar into oil, asphaltenes and preasphaltenes. The first two fractions separated again by silica gel LC into aliphatic, aromatic, polar subfractions. Each subfractions were then characterized by ^1H NMR and IR spectroscopies and capillary GC. Whitehurst et. al. (1982) combined LC, GC, and field ionization mass spectroscopy (FIMS) to characterize the SESC fractions of coal-derived liquids. Collin et al. (1983) characterized distillable fraction obtained from hydrogenation by GC-MS and NMR. Philip and Anthony (1982) separated coal derived liquids by GPC into aromatic, phenolic, and asphaltenic factions then first two were characterized by GC-MS. Young et al. (1983) employed IR, hydrogen NMR and viscometer to analyzed SRC-II and H-coal liquids. These liquids were also separated by

ion-exchange LC, silica gel column LC. Few fractions were characterized by GC-MS, or capillary GC. Ignasiak et al. (1983) separating asphaltene by GPC into five fractions. Every fraction underwent VPO, FTIR, hydrogen NMR, ^{13}C NMR, thermogravimetric analyzer (TGA), pyrolytic chromatograph for study of their relative polymer-forming propensity. Yokoyama et al. (1983) studied the chemical structure of the benzene-soluble fraction of heavy oil from coal hydrogenation by separating the benzene-soluble fraction by acid-base extraction, silica gel column LC, and GPC, then analyzed by hydrogen NMR and VPO. Koplick and Wails (1983) divided flash pyrolysis tar into asphaltenes, maltenes, preasphaltenes and residues. The maltenes fraction then underwent ion-exchange and adsorption chromatography, each subfraction then analyzed by VPO and GC-MS. Seshadri and Cronauer (1983) divided coal derived products of the SRC-II liquefaction by solvent extraction or by distillation into different fractions. The middle and heavy distillates were separated again by SESC, each subfraction were examined by carbon NMR and FTIR spectroscopic methods.

The liquids generated by coal processes and related fuels (i.e. crude oil, oil sand , asphaltenes etc.) are among the most widely studied complex mixtures of organic compounds. However, the results obtained by different researchers in the field are difficult to compare due to the use of different procedures or different analysis conditions with the same procedures.

Chapter III

EXPERIMENTAL

3.1 PRELIMINARY ANALYSIS

The pyrolysis experiments of this part of the research were performed on the existing flash tube reactor at the Clean Fuels Institute of City College of New York (Graff et al. 1976, Dobner et al. 1976, Chen et al. 1983). The analysis of the gas product, namely methane, ethane, propane and benzene, toluene and xylene (BTX) was achieved by on-line mass spectrometry. The yield of solid product, char, was measured by the carbon dioxide obtained in the combustion of residual char with oxygen. Liquid product heavier than xylene was determined by difference.

To have better information on the liquid products, the reactor system was modified by inserting a liquid collecting tube. A 3.2 mm i.d. stainless steel tube packed with alumina and immersed in liquid nitrogen was added between the tube reactor and the expansion coil (Figure 1). To find the effectiveness of this modification a few runs were made. The gas products passing through this trap were analyzed by on-line mass spectrometry.

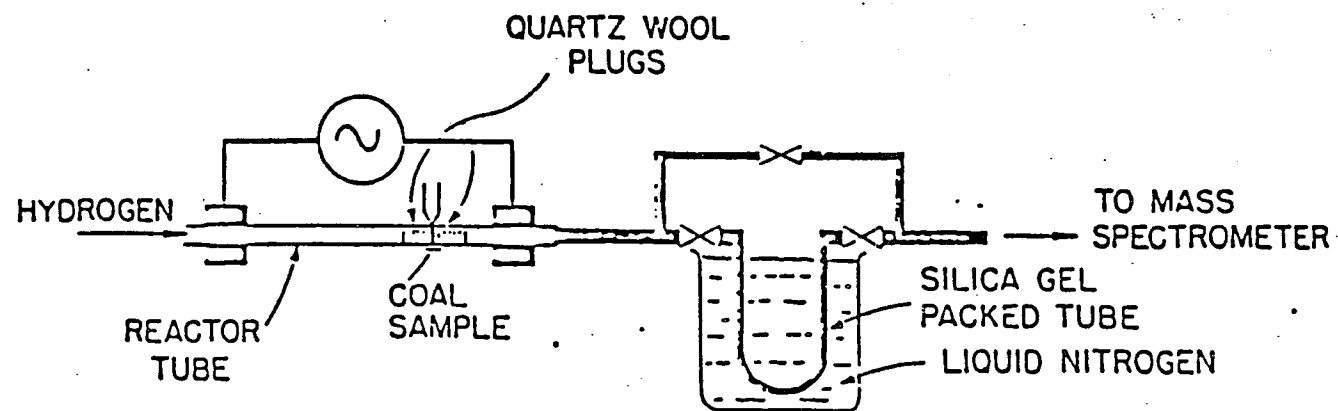


Figure 1

Experimental Arrangement Used in the Trapping
of Liquids Produced During Flash Hydrogenation

Figure 2 shows a comparison of the mass spectrometer responses for methane and benzene with and without trapping. Even species as light as methane were successfully trapped. Liquids were collected for coal reaction conditions of 100 atm. of hydrogen, 0.6 seconds vapor residence time and a variety of temperatures.

Following each run the trap was closed at both ends, allowed to reach room temperature and weighed. The contents of the tube were eluted with 2 ml of chloroform followed by 5 ml of pyridine. Each fraction was kept separately in a sealed vial and stored in a freezer for subsequent analysis. The internal walls of the reactor and connections between the reactor and the trap and also between the trap and the mass spectrometer were rinsed with pyridine. These solutions were then combined with the pyridine-soluble fraction which eluted from the trap.

The chloroform-soluble fraction was analyzed by gas chromatography with a Hewlet Packard model 5730 using a 360 cm x 2 mm i.d. glass column packed with 3% OV-1 on Chromosorb W-HP 80-100 mesh. The initial temperature of 25 C was held for 5 minutes and then raised at 8 C/min to 220 C. Injection temperature was 290 C, and detectors were held at 260 C. Identification of compounds was performed by comparison of the retention times of the unknowns with standards.

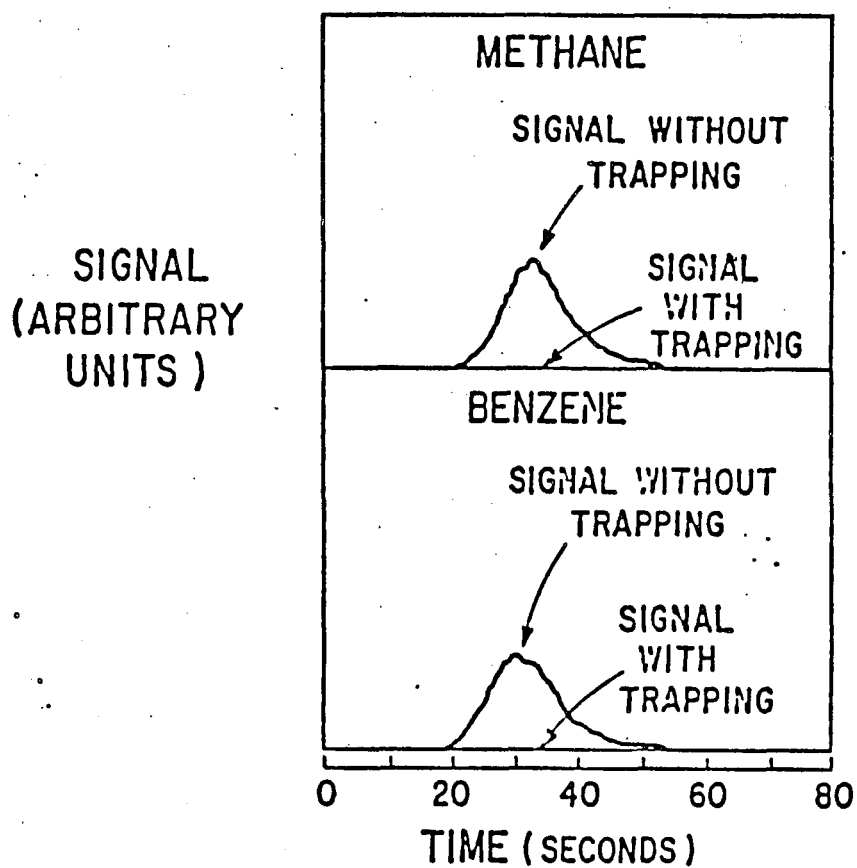


Figure 2

Mass Spectrometer Trace verifying
Trapping Efficiency.

The pyridine-soluble fraction did not show any peaks in the gas chromatograph, and, consequently, was assumed to consist mainly of heavy species not eluted from the gas chromatography (GC) column. Pyridine-soluble fractions were processed in a rotary evaporator to eliminate solvent and then weighed.

3.2 HPLC DEVELOPMENT

The size of the coal samples used for the above runs were about 10 mg. The amount of liquid products obtained, which was less than 4 mg was proved too small to be analyzed with accuracy. Since HPLC is amenable to work with small samples, we turned our attention to the development of the techniques described below. Silica gel was found to be a better separation medium than activated alumina for coal liquids. The reaction system was modified to accommodate a larger coal sample (about 25 mg). The products were carried as vapor through a heated line, into a silica gel packed column immersed in liquid nitrogen, where the liquids were trapped quantitatively. The efficiency of trapping by this arrangement was monitored in every run with the aid of the on-line mass spectrometer. This sampling tube was then connected to a solvent-elution system (Figure 3) and the solvent-elution procedure started.

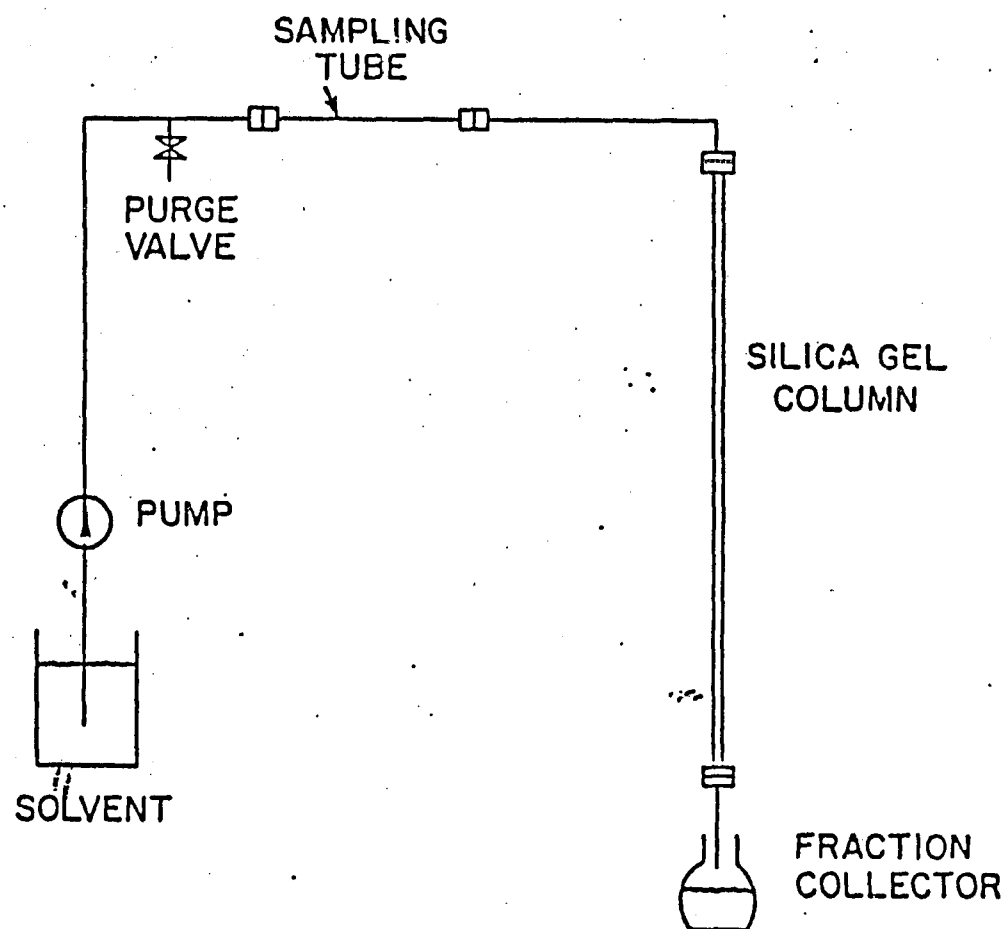


Figure 3 Solvent elution liquid chromatograph.

The sample tube acted as an injection loop in this system. Separation was carried out on a 100 cm. x 0.63 cm i.d. stainless steel column packed with silica gel. The sequence of solvents used, which had been determined by previous experiments using thin layer chromatography(TLC), was: hexane, chloroform, tetrahydrofuran with 3% ethanol and pyridine. The hexane and chloroform fractions were analyzed by GC with a 3% OV-1 column using the temperature program described above. Other fractions (eluted by THF and pyridine) were too heavy to be eluted and separated by GC. The solvents for these fractions were evaporated using a rotary evaporator and the weight of residues recorded.

Liquid products taken from the bench scale flash hydrogenation reactor (as described above) were analyzed by HPLC in an Altex model 312 high performance liquid chromatograph. Two different types of columns were tested:

(1) Reverse Phase column - C18 Lichrosorb; the analysis was performed using a gradient concentration program (the solvents were water-methanol and chloroform-methanol mixtures). Good separation and elution of polycyclic aromatics was obtained, but heavier and polar compounds were not eluted.

(2) Normal Phase column - Lichrosorb 60 column; using chloroform as solvent, the elution of polycyclic aromatics was obtained. However, it could not separate polar compounds well and some of the polar compounds appeared as a single, large peak.

3.3 ANALYSIS OF FLASH STEAM PYROLYSIS LIQUIDS

Flash hydrolysis refers to the flash heating of raw coal in steam at elevated pressure with controlled vapor product residence times. In this part of the research, flash hydrolysis was studied over a range of operating conditions. The reactor (figure 4) was described elsewhere (Graff et al. 1983). The liquids trap was constructed of 12 meter of 6.25 mm ID. stainless steel tubing wound into a coil and installed between the reactor and the main flow control valve (figure 5). The trap was maintained at 500 C using band heaters and had a volume equivalent to 30 seconds of steam flow. The reactor system was brought to the desired steady temperature with the entire flow of steam passing through both the reactor and the trap. Coal was injected into the reactor with a helium pulse and 30 seconds later the trap was sealed with air-operated valves located at each end of the trap.

The liquids were recovered from the coil using THF as a solvent. The solvent was pumped through a column containing activated alumina to eliminate peroxides before being passed through the sampling coil. The solvent containing the coal-derived liquids was collected in a flask under inert atmosphere to avoid oxidation of the liquids or solvent.

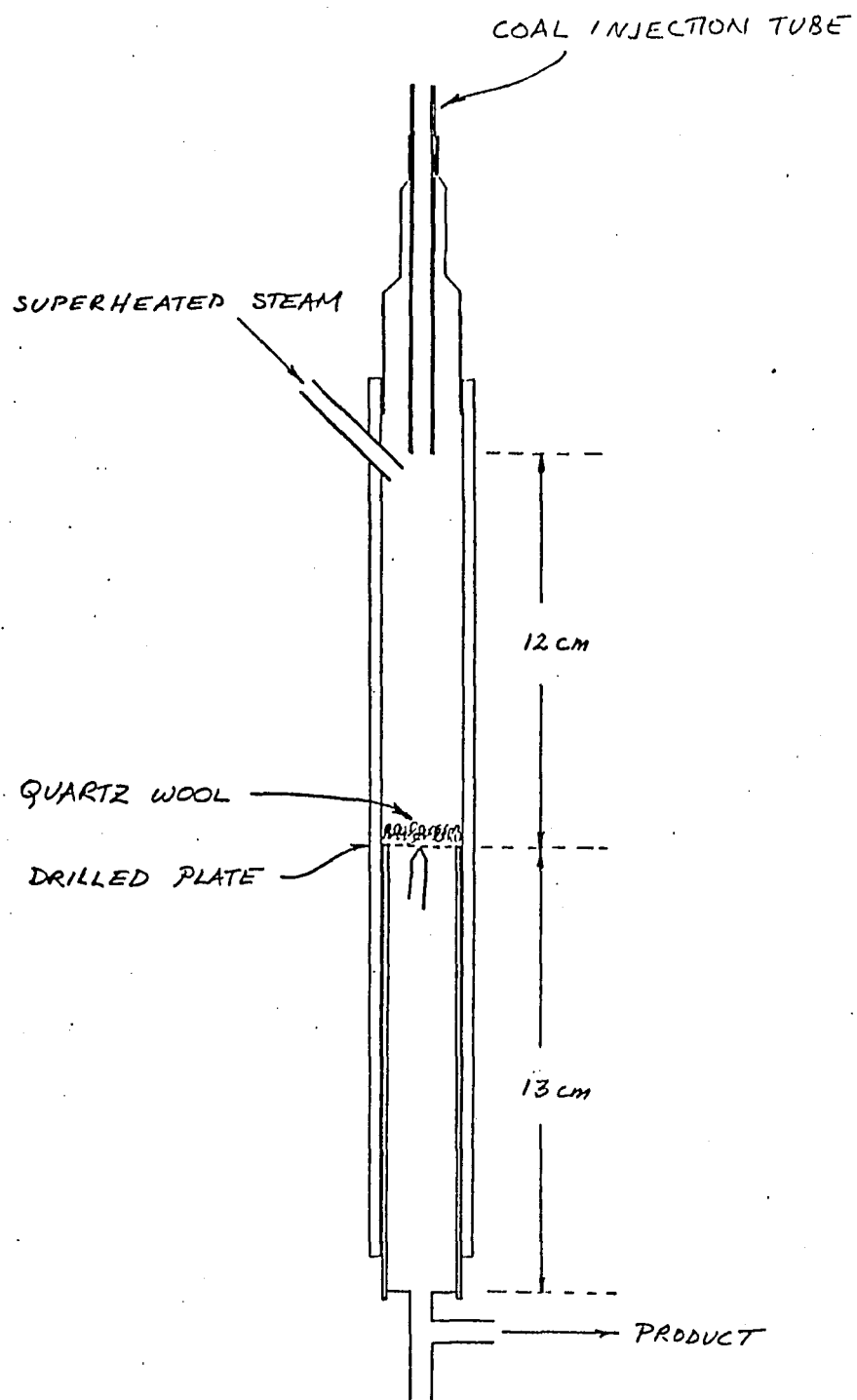


Figure 4

Modified Flash Hydrolysis Reactor

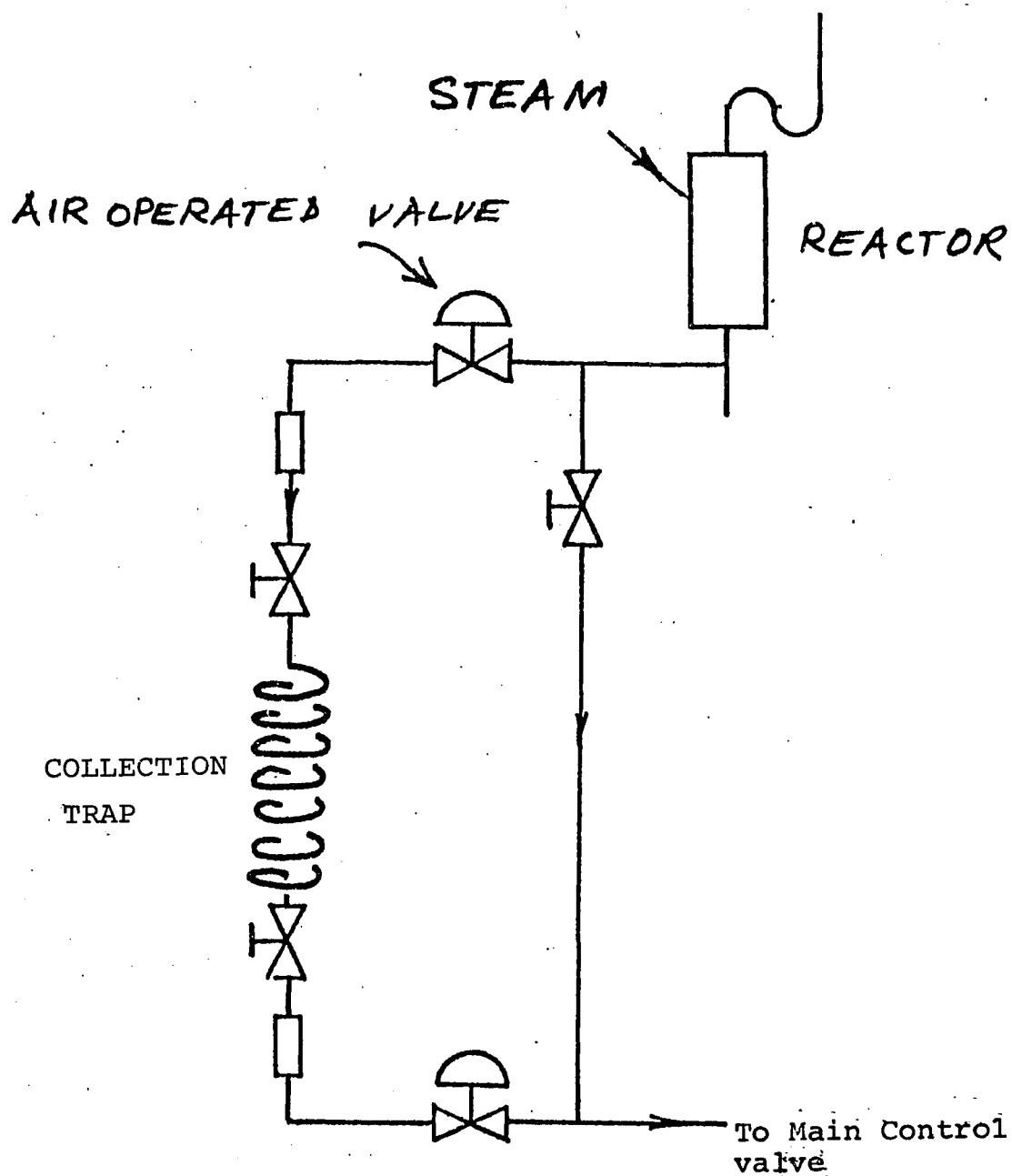


Figure 5: Schematic Diagram Showing Installation of Collection Trap.

The liquids were separated from the solvent by vacuum vaporization for thirty minutes at 45 C in a rotary evaporator or vacuum oven. Samples were weighed to determine the total mass of liquid present.

Automatic Modified SESC System

The original sequential elution with selective solvents chromatography (SESC) technique was developed by Farcasiu (1977). The purpose of SESC was to use a series of elution solvents which would separate specific classes of components from Solvent Refined Coal by polarity and functionality. Farcasiu (Whitehurst, et al. 1976, and Farcasiu, 1977) proved by TLC that each SESC fraction, and only that fraction, represents the given functionality. This technique was adopted with minor modification to separate liquids obtained from coal flash hydrogenation in this laboratory.

An automatic modified SESC analysis system was designed. Figure 6 shows the arrangement. The solvents to be used were stored in a set of containers which were connected to solenoid valves separately. The normally closed solenoid valves were used to allow the passage of one solvent at a time to the HPLC pump.

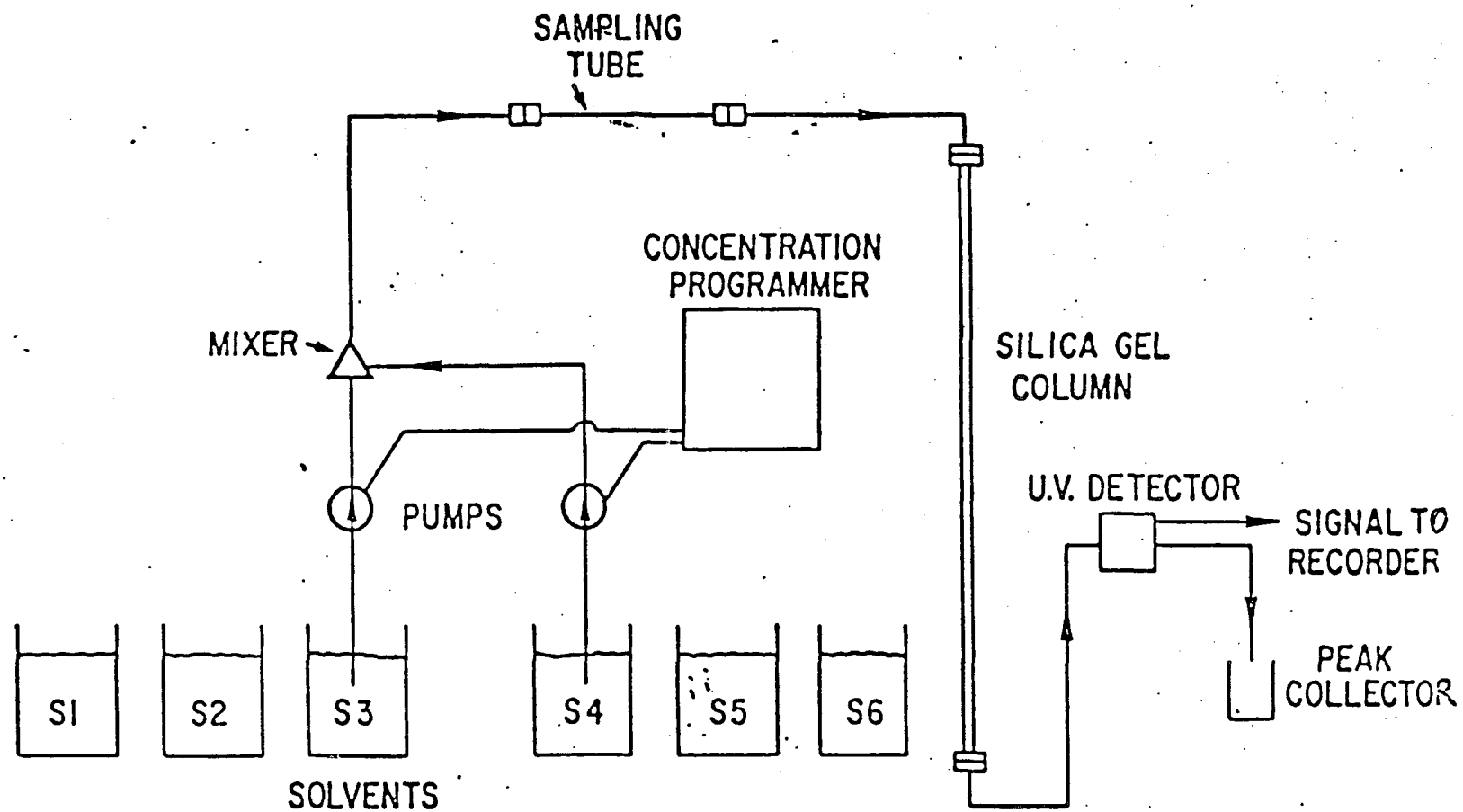


Figure 6: Automatic Modified SESC Analysis System.

A cam-timer programmer controls the timing and sequence of solvents passing through an HPLC sampling valve and the separation column. The elution of the fractions was monitored with an U.V. detector and the fractions were collected by an automatic fraction collector. Solvents that absorb in the range of the U.V. detector of the Altex model 312 were eliminated from Farcasiu's SESC solvents sequence. Also, in order to avoid a sharp transition between solvents, a concentration gradient linear program was used to change from one solvent to another.

The silica gel used here was prepared in the following way: first, the silica gel was washed with methanol and vacuum dried. Air was passed through a water containing flask at 26 C then through a flask containing dried silica gel to adjust the water content of silica gel to 4 %. The prepared silica gel was packed into coiled stainless steel tubing (6.3 mm x 100 cm). After each run the separation column was discarded.

The first solvent in the series, hexane, was passed through the column before sample injection. The coal liquids were dissolved in THF, and then injected into the separation column using a HPLC injection valve. The whole series of solvents were then passed through the system at a flow rate of 1.5 ml/min, giving 20 minutes for each solvent. The sequence of the solvents is : hexane, hexane with 15%

benzene, chloroform, chloroform with 10% ether, ether with 3% ethanol, methanol, chloroform with 3% ethanol, and THF with 3% ethanol. The eluent from the separation column was passed through the U.V. detector at 254 nm., then sent to a fraction collector. The peaks indicated by the detector were collected and weighed after evaporation of solvent under nitrogen.

The operation of the total system (including solvent pump, timer programmer, solenoid valves, solvent containers and connecting lines, silica gel liquid chromatography column, U.V. detector, recorder and fraction collector) was tested several times without sample. The programmer accuracy and the operation of the automatic modified SESC system were found acceptable.

Then the automatic modified SESC system was tested with coal liquids. Hydrocarbonization oils from Union Carbide were used for checking the reproducibility. In figure 7, for the same coal liquid, with different sample size, similar weight distribution curves were obtained.

After the solvents in each fraction were vaporized, the total residual mass of one run was found to be greater than the original sample weight. The extra weight was found in the THF fractions. The removal of the THF solvent was not quantitative.

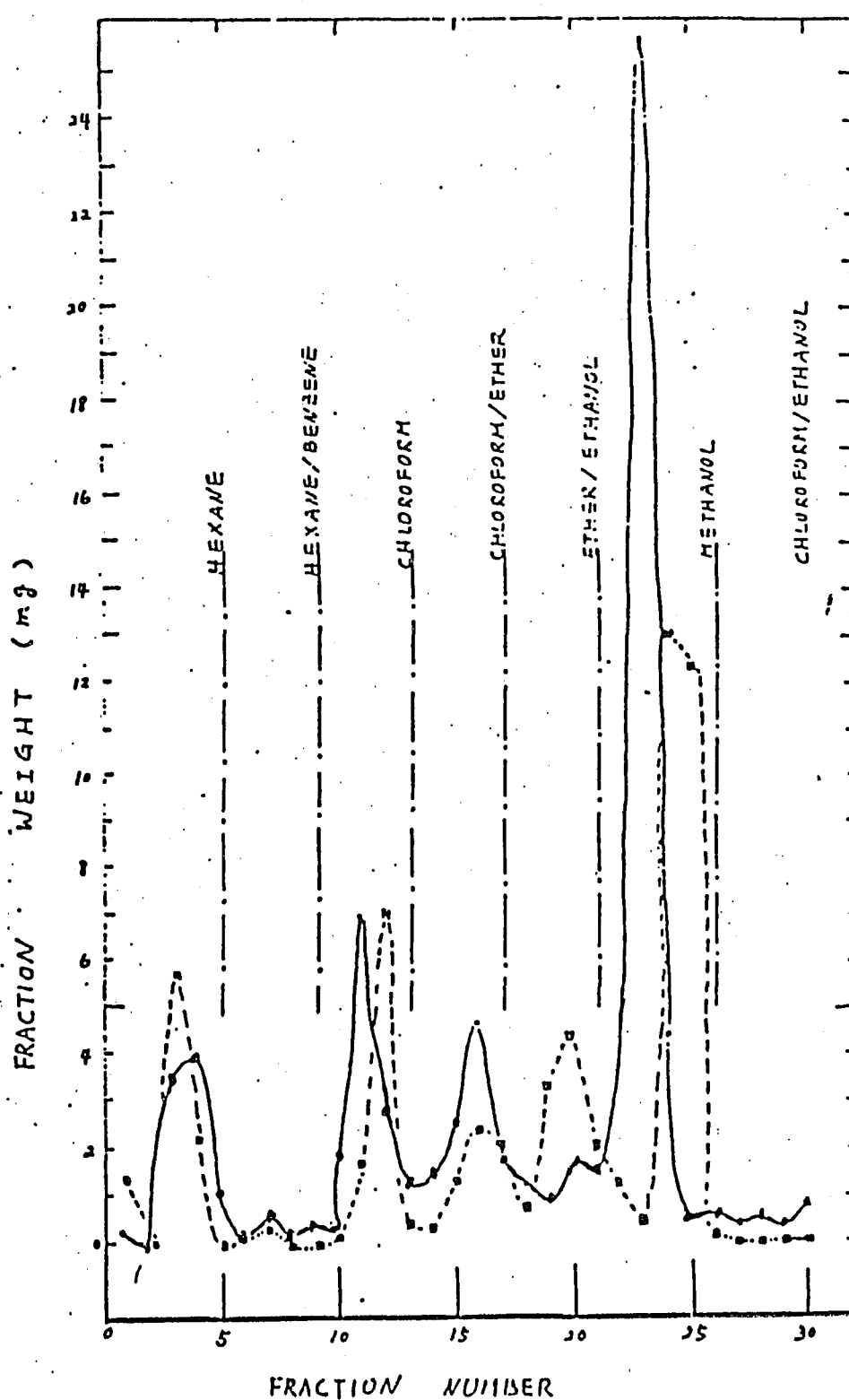


Figure 7: Modified SESC fractionation of Hydrocarbonization Oils

This problem of incomplete elimination of THF was considered. After consultation with other workers in this field, we reached the conclusion that THF reacted with oxygen from the air very easily, to form peroxides. These peroxides react with the coal liquids and therefore cannot be separated from the sample.

A method to eliminate peroxides and avoid subsequent oxidation of the THF is to pass the solvent through a column of activated alumina to adsorb the peroxides. Also, further contact of THF with air has to be avoided.

Tests were performed using samples of coal liquids of known weight dissolved in peroxides-free THF. The absence of peroxides in THF was tested by adding a solution of KI and starch to a small amount of solvent. Elimination of peroxides by adsorption on activated alumina was found to be complete.

Comparative Modified SESC Analysis of Coal Liquids From Different Source

Three different coal liquids were run to test the automatic modified SESC system, and the weight distribution for each coal liquid was found to be different (Table 1).

Table 1 Distribution of Modified SESC of different coal liquids

Fraction solvent	Hydrocarbonization Oils (Union Carbide)		Hydropyrolysis Oils (Cities Service)	Flash Hydro- genation Oils (City College)
	(1)	(2)		
Hexane.	14.53	10.19	3.48	9.02
Hexane/ 15% Benzene	1.02	2.01	8.34	15.69
CHCl_3	14.53	14.72	6.45	10.98
CHCl_3 /Ether	9.94	13.58	29.31	18.82
Ether/etOH	16.67	7.30	10.62	11.37
MeOH	42.51	49.18	23.48	25.10
CHCl_3 /etOH	0.80	3.02	18.32	9.02

Both the flash hydrogenation liquids and the hydrocarbonization oils have almost 50% of total weight (not including the residual of THF fraction) in the methanol fraction which is assumed to contain highly polar substances. The hydropyrolysis oils have only 20% of the total weight in the methanol fraction, and have 25% in the CHCl_3 /ether fraction which should contain one atom of oxygen as phenolic -OH per molecule and one pyrrolic nitrogen in every two molecules (Farcasiu, 1977). On the other hand, hydrocarbonization liquids have only about 10% of the total weight in the CHCl_3 /ether fraction.

Hydrocarbonization oils have about 15%, flash hydrogenation liquids about 5% and the hydropyrolysis oils only 3% of the total weight in the hexane fraction. In the hexane with 15% benzene fractions, both the flash hydrogenation liquids (7%) and the hydropyrolysis oils (8%) have higher percentage than the hydrocarbonization oils (1%).

These differences may reflect different processing variables and/or differences in the starting coals themselves.

Liquid Collection from Flash Hydrolysis

The coal sample size used for flash hydrolysis was increased to about 100 mg, and reacted in the system

described in section 3.3. The coal derived liquids were recovered from the trap using THF as a solvent. THF was pumped through a column containing activated alumina to eliminate peroxides before being passed through the sampling coil. The eluent now containing the coal derived liquids was collected in a flask under inert atmosphere to avoid oxidation of the liquids or solvent.

The solvent was then evaporated under vacuum at 68 C using a rotary evaporator.

Elemental Analysis

A Perkin-Elmer model 240B elemental analyzer was used for the determination of carbon, hydrogen and nitrogen in coal and coal liquids. Acetanilide was used as the main calibration standard on the basis that the carbon and hydrogen contents were similar to those of typical samples being analyzed. The preweighed sample (1 - 3 mg) was combusted in oxygen at 980 C during the determination of carbon, hydrogen and nitrogen. The combustion products were flushed with helium through finely ground cuprin, where nitrogen oxides were reduced to nitrogen and excess oxygen was absorbed as oxide. The remaining gases then mixed with helium to a homogeneous equilibrated mixture at fixed pressure and temperature. The gas mixture was sent to the detection system comprising three pairs of thermal conductivity cells in series. The platinum filaments of

each cell pair are connected differentially in a bridge circuit so that any difference in the contents of the two cells will result in an electrical signal. A magnesium perchlorate trap between the first pair of thermal conductivity cells adsorbs any water from the gas mixture before it enters the second cell so that the signal obtained from the corresponding bridge circuit is proportional to the amount of water removed. Likewise, an adsorbing trap between the second pair of cells results in a signal in proportion to the carbon dioxide removed from the sample. The last pair of cells detects nitrogen by comparing the thermal conductivity of the remaining sample gas with that of pure helium. In each case pure helium provides the background signals, thereby several blanks and determinations of standards were carried out each working day. The elemental analyzer (Perkin-Elmer 240B) was tested with calibration standards and some coal samples. The results are reproducible and in good agreement with analysis performed in other laboratories. Duplication tests with coals and also with carbon black showed a reproducibility of + 1.0 %.

In table 2 analytical results obtained with the elemental analyzer are compared to those from outside sources. Most of the data show good agreement, only for the carbon content of the PSOC 22 coal our results and those from Robinson Laboratories (63.58% and 60.45%) are slightly different from those from Pennsylvania State University (70.53%).

Table 2 Analytical results based on Elemental Analyzer

sample ⁺	sources	C	H	N	Ash
		content (%)			
ILL#6 coal	CUNY	65.20	4.51	1.14	12.24
	Smith, Rudy & Co.	66.30	4.98	1.16	12.77
PSOC-265	CUNY	70.14	4.02	1.10	15.10
	P.S.U.	71.47	4.44	2.03	15.54
	Robinson lab.	70.05	4.45	1.29	16.76
PSOC-22	CUNY	63.58	4.03	1.18	12.32
	P.S.U.	70.53	5.12	1.39	10.14
	Robinson's lab	60.45	4.26	1.02	12.33
PSOC-265 HF*	CUNY	81.83	4.48	1.51	2.14
	Robinson's lab	82.07	5.14	1.54	1.84
PSOC-22 HF*	CUNY	73.57	4.30	1.37	0.66
	Robinson's lab	73.54	4.75	1.30	0.78

⁺ All the coal samples are on dry basis

* after HF treatment

Molecular Weight Distribution Curves

The molecular weight distribution of the samples collected by modified SESC was determined by steric exclusion chromatography. Steric exclusion chromatography is a non-interactive mode of separation based on the size and shape of the molecules in the sample. As the sample molecules pass through the column, they are sorted by the pores of the column packing material. Larger molecules cannot diffuse into the pores of the packing material, and hence elute faster than smaller molecules which permeate the pores of the resin and are retained in the column longer. The retention volume V_R can be expressed by the equation:

$$V_R = V_M + KV_S.$$
 Here the mobile-phase volume V_M and the stationary-phase volume V_S are the void volume and the total pore volume of the packing materials, respectively.

The distribution constant K depends on the molecular size of the sample and the pore size of the gel, not on the chemical nature of the sample. Small molecules that can enter into the pores freely have $K=1$, whereas very large molecules that are completely excluded from all pores have $K=0$. Molecular size is associated with and identified by the particular elution volume at which a given molecule emerges. A plot of elution volume versus the log of molecular weight is a straight line within a suitable

molecular weight range. The relation can be expressed by the following equation:

$$V_R = A + B * \log (MW)$$
 where A and B are constants. The curve obtained is used for calibration.

Two Altex μ -spherogel 50 A and 100 A (8mm ID x 30cm L, prepacked by Altex Co.) steric exclusion HPLC columns connected in series were used for this molecular weight distribution analysis. The column was calibrated using polystyrene polymer standards (Mn: 17500, 9000, 4000, 2000 with Mw/Mn smaller than 1.06 from Pressure Chemical Co., and Mn 2850 with Mw/Mn smaller than 1.10 from Polymer Lab. Ltd., also Mn 970, 500 and styrene monomer Mn 104.15 from Altex Co.) and aromatic hydrocarbons (hexaphenylbenzene MW 534.7, 1,2,3,4-tetraphenyl-1,3-cyclopentadiene MW 370.5, coronene MW 300.36, 2,3-benzanthracene MW 228.29, chrysene MW 228.3, stilbene MW 180, anthracene Mw 178, xylene Mw 106, ethyl-benzene MW 106, and benzene Mw 78). The detector was a U.V. absorption unit with filter to operate at 254 nm. No correction of the detector reponse was attempted and the results are presented as relative response of the detector vs. molecular weight. Calibrations were carried out daily. An example is given in Figure 8.

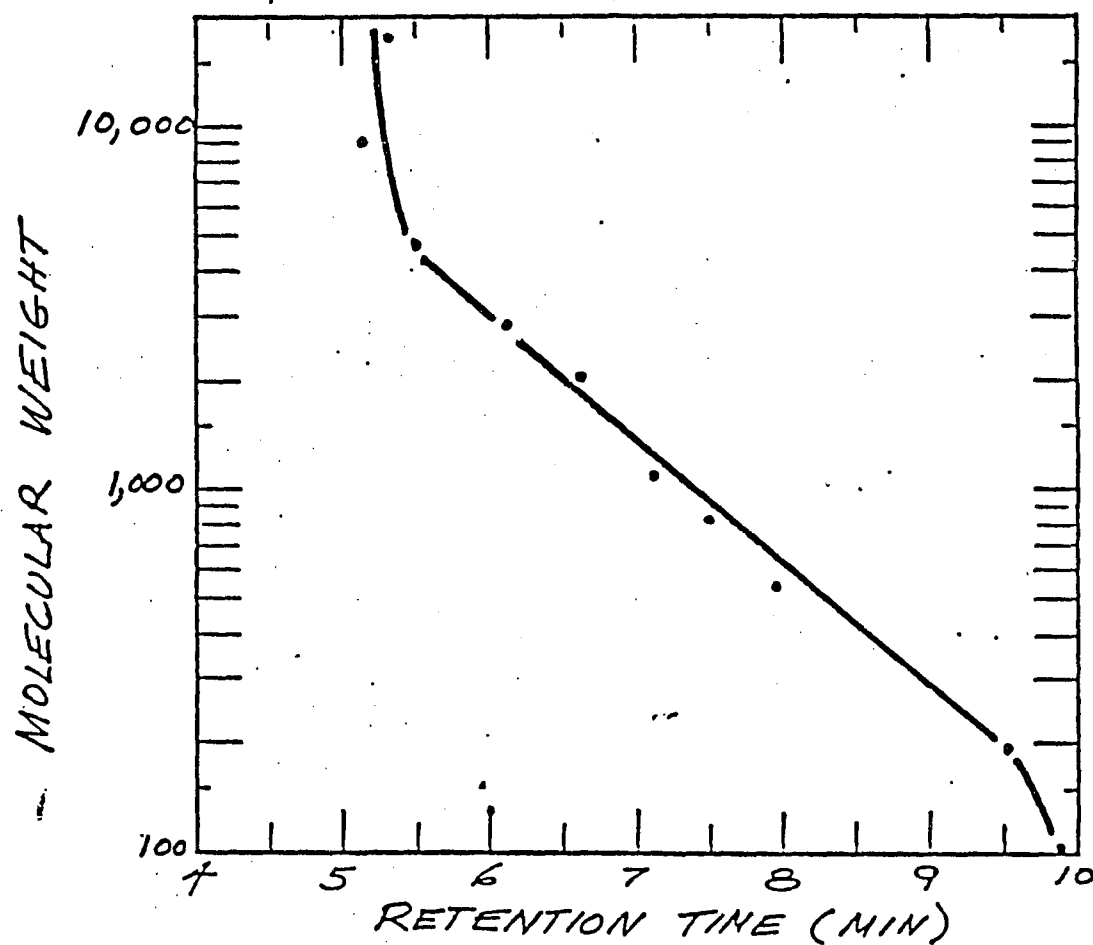


Figure 8 Calibration of Steric Exclusion Chromatography Column (100 Å μ -Spherogel) with Polystyrene Standards and aromatic hydrocarbons.

3.4 COMPARISON OF HELIUM/STEAM PYROLYSIS AND HYDROPYROLYSIS

As mentioned before, the purpose of this part of research was to find the properties of the heavier liquid from coal hydrolysis. Another objective was to compare the nature of the yields obtained by using either hydrogen or steam when flash pyrolyzing coal. Since the amount of the coal liquids produced under steam pyrolysis in our laboratory was scant for more detailed analysis, Cities Service R&D Co. provided coal liquids of run WKB-68 and WKB-77 from its pilot plant to us. In the Cities Service R&D plant, coal was treated under identical reaction conditions, except that one sample was reacted under hydrogen, and the other using steam/helium atmosphere.

The coal used was Western Kentucky bituminous No. 9 (from the Pyro Mine, West Virginia) crushed in size smaller than 297 μ m with all but 10 percent of the particles smaller than 74 μ m removed. The composition of the coal provided by Cities Service R&D Co. is given in table 3.

The pyrolysis system of Cities Service Co. shown in Figure 9 was operated at 6.89 MPa with pure hydrogen or a mixture of 7.6 mole percent of steam in helium. Coal was fed at a rate of 1 Kg/hr into the reactor which was 7.9 cm in diameter and 100 cm long. All the tests were conducted at 740 C in a hot zone of 30 cm in length.

Table 3

Composition of Western Kentucky No. 9 CoalWeight Percent

C	74.17
H	5.12
N	1.19
S	2.64
O (by difference)	7.31
Ash (MF)	9.57
Volatile matter (MF)	35.30
Fixed carbon (by difference) moisture	55.13

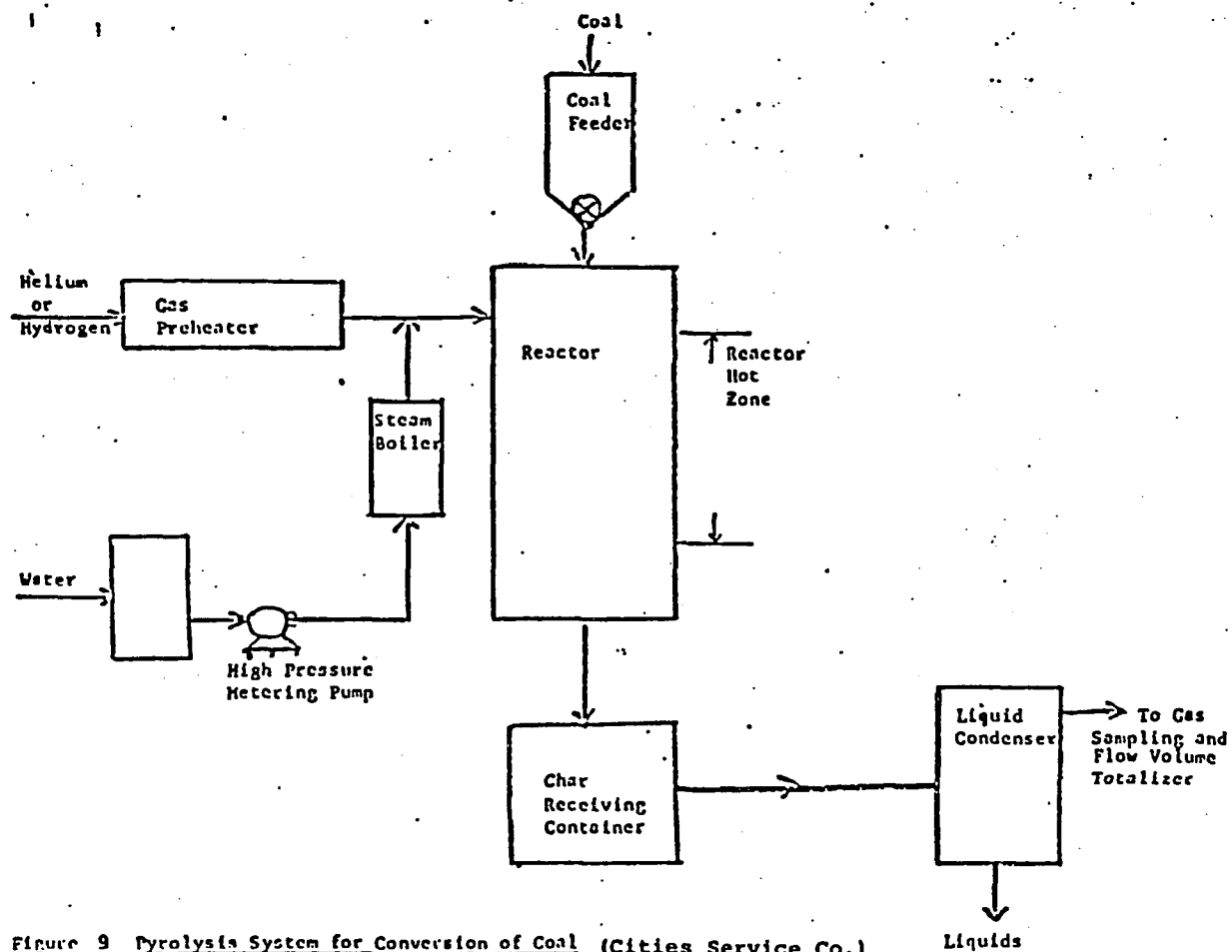


Figure 9 Pyrolysis System for Conversion of Coal (Cities Service Co.)

The superficial velocity of the gases fed into the reactor under these temperature and pressure conditions varies from 5 to 8 cm/s. The free falling coal particles are maintained in the hot reactor zone one second. The gas residence time is 12.3 seconds for the hydrogen run, and 18.9 seconds for the steam/helium run. Full details of this apparatus are described elsewhere (Fling et al).

Elemental analyses of liquid and solid reaction products were performed by Cities Service R&D Co. with a CHN Perkin-Elmer model 240 apparatus as per ASTM D3178. Analyses of gaseous products were performed with a Perkin-Elmer model 3920 chromatograph with dual Chromosorb 102 columns, with dual thermal conductivity and flame ionization detectors.

The samples provided to CCNY were:

- (1) WKB-68 poured liquids
- (2) WKB-68 char
- (3) WKB-77 poured liquids
- (4) WKB-77 acetone wash liquids
- (5) WKB-77 char

Run WKB-68 was performed using pure hydrogen as the reacting gas. A mixture of steam and helium was used in run WKB-77.

Analyses performed on the liquid samples include the following:

- a) modified SESC fractionation: The three liquid samples provided were fractionated.
- b) elemental analysis: C, H, and N analysis were performed on all samples and modified SESC fractions, as well as on the solid samples.
- c) boiling point distribution curves (G.C. method): were obtained for WKB-68 and 77 poured liquids, for modified SESC fractions 1, 2, 3, and 4 of the poured liquids of WKB-66, and modified SESC fractions 1, 2, 3, and 4 of WKB-77 poured liquids.
- d) molecular weight distribution curves: They were obtained by steric exclusion HPLC for both samples and all the modified SESC fractions.
- e) H-NMR spectroscopy: was used to characterize WKB-68 liquid, WKB-77 acetone wash liquid, WKB-77 liquid, also all the modified SESC fractions of WKB-68 and 77 liquids.

The above analyses procedures are described in more detail below:

- a) Modified Sequential Elution with Selective Solvents Chromatography. In the modified version of SESC used here, 1.5 g of sample was dissolved in dichloromethane

and mixed with a mixture of silica gel and sand of 1:1 ratio. The solvent was eliminated using a rotary evaporator and the sample (included now in the sand/silica gel mixture) was placed on the top of a 1.0 cm i.d. x 100 cm stainless steel column which was packed with activated silica gel.

The silica gel packing of the column was activated by washing silica gel (Fisher reagent A.C.S., 100 to 200 mesh) with 1.3 N HCl in 22 percent water/78 percent methanol to increase its acidity. It was then washed with methanol and dried at 120 C. The final moisture content of the silica gel was adjusted to 4 percent by passing a controlled temperature air stream saturated with water over the silica gel.

After the sample was introduced into the column, the solvent sequencing began. The solvent flow rate was 1 ml/min and the fractions were eluted successively with the following solvents: hexane, hexane/15% benzene, chloroform, chloroform/10% diethyl ether, diethyl ether/3% ethanol, methanol, chloroform/3% ethanol and tetrahydrofuran (THF) with 3% ethanol. The ninth fraction in Farcasiu's sequence uses pyridine with 3% ethanol. This fraction was not eluted in our work.

The eluents were collected in 25 ml portions. The solvent was vaporized in a rotary evaporator and the net

weight of the residue was then plotted vs. time. When the net weight of the residue of a portion appeared to be the end of a peak, the eluent used was stopped and the next eluent was used. Usually the volume of each eluent was about 250 ml to 300 ml for this set of experiments.

After the fractions were collected and solvents were evaporated, then the sample was at room temperature and under vacuum (about 1.5 - 2 mm Hg) for twenty-four hours (except for fraction VI), the net weight of each fraction was obtained and the weight percent of the original sample was calculated for comparison. The fractions were then used for further analysis.

b) Elemental Analysis. Elemental analyses were performed with a Perkin Elmer 240B Elemental Analyzer.

c) Boiling point distribution curves(G.C. method). Boiling point curves were obtained using a Hewlett-Packard 5750 research GC with flame ionization detector and a Hewlett-Packard 3380A integrator. The samples were analyzed on two 3% Dexil 300 on Chromosorb WA-W columns which were calibrated with n-paraffins and aromatic hydrocarbon standards. The temperature program of the gas chromatograph was from 50 C to 350 C, at a rate of 8 C/min. Helium was used as a carrier gas.

d) Molecular Size Distribution. Molecular size distributions were obtained as described in section 3.3 using the steric exclusion HPLC Altex model 312 high performance liquid chromatograph, equipped and calibrated as described before.

e) H-NMR Spectroscopy. All NMR spectra were run on a Varian EM-360 60 MHz proton NMR spectrometer. Scan time was 10 minutes with a sweep width of 10 ppm. The internal standard was tetramethylsilane. Solvents used were deuterated chloroform and deuterated pyridine. Both solvents were 98% purity, provided by Sigma Chemicals.

Chapter IV

RESULTS AND DISCUSSION

4.1 LIQUID ANALYSIS

4.1.1 Preliminary Results

The liquid product collected from some of the flash hydrogenation runs (described in section 3.1) were eluted with chloroform and pyridine. The chloroform eluted fractions were analyzed by GC. A typical chromatographic trace is given in Figure 10. Chloroform eluted species amount to a maximum of 4.5% of the total carbon at a reaction temperature of 760 C (Figure 11). The main constituents of this fraction are naphthalene, ethylbenzene, diphenyl, fluorene, anthracene, fluoranthrene, pyrene, and chrysene. The calculation of composition of the chloroform soluble fractions was performed by a computer program and the information was stored. A sample printout is given in table 4.

The product fraction which is not eluted with chloroform but eluted with pyridine did not show any peaks in the GC analysis. It was consequently assumed to consist mainly of heavy species that do not elute from the GC column. Pyridine-soluble fractions were processed in a rotary evaporator to vaporize the solvent, and weighed.

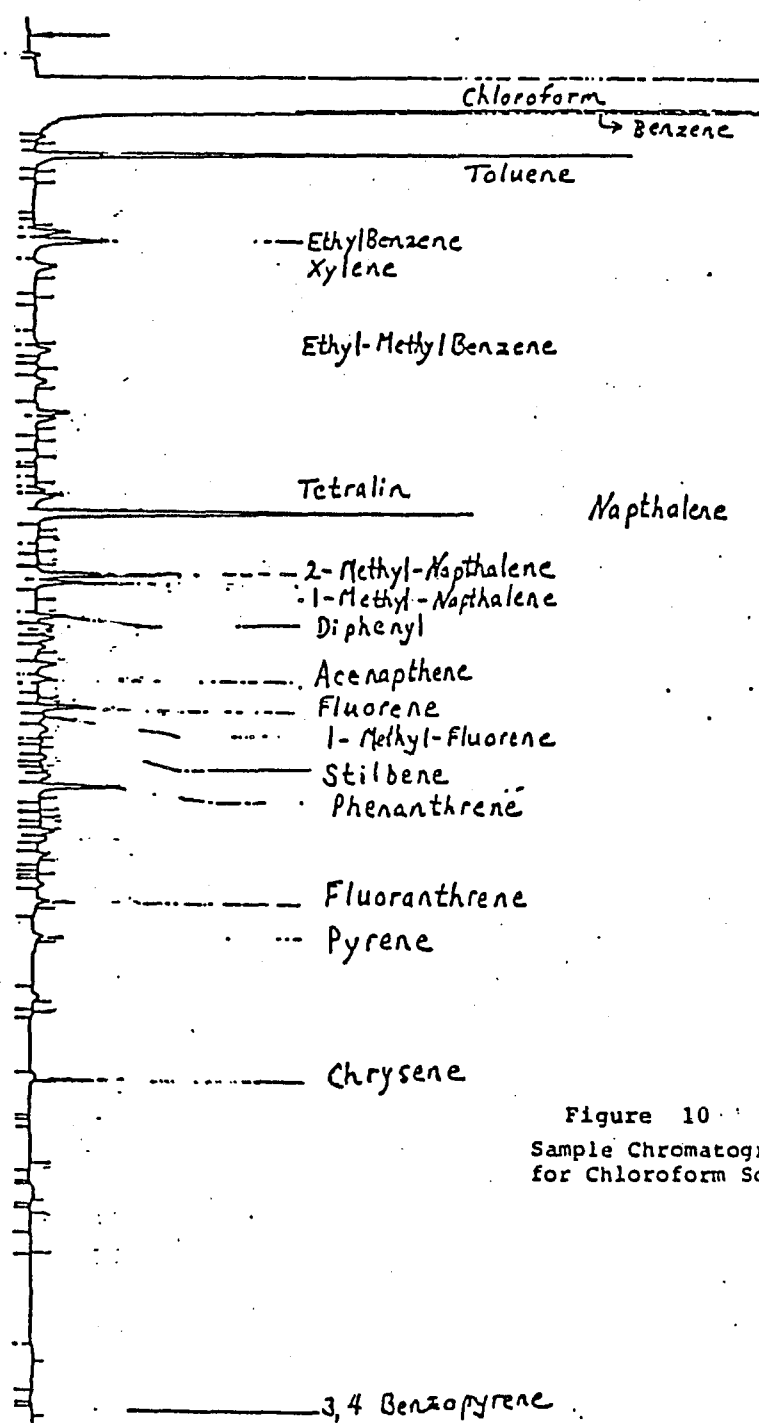


Figure 10
Sample Chromatographic Trace
for Chloroform Soluble Sample.

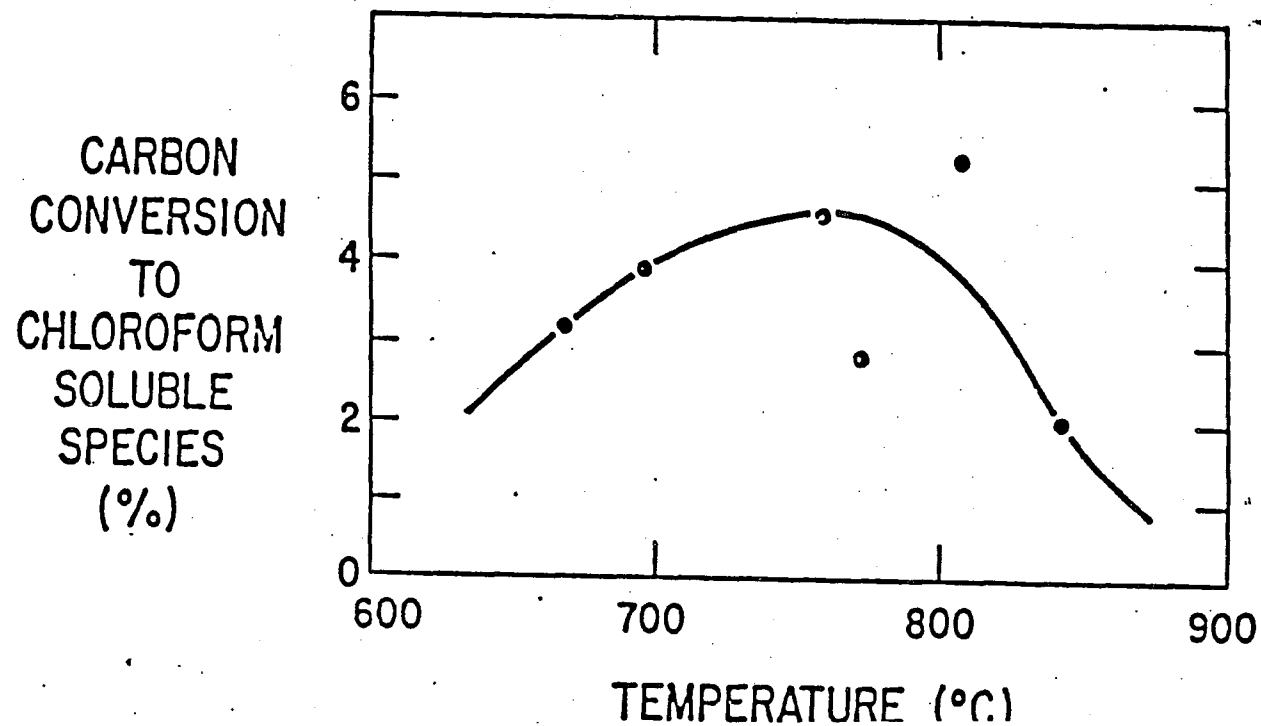


Figure 11 Carbon Conversion to Species Heavier than xylene and soluble in chloroform. Pittsburgh No. 8 coal, 100 atmospheres, hydrogen, 0.6 second vapor residence time, 10 seconds solids contact time, heating rate 650°C per second.

TABLE 4

SAMPLE PRINTOUT OF COMPUTER PROGRAM FOR ANALYSIS
OF CHLOROFORM SOLUBLE FRACTION BY GAS CHROMATOGRAPHY

RUN FILE - IR152
 TYPE OF COAL - IRELAND MINE
 MASS OF COAL - 20.34 MG
 %C IN COAL - 69.6
 MG. OF C IN COAL - 14.156
 TEMP OF RUN - 807 (MAX 818) DEGREES C.
 PRESSURE - 100 ATM.
 RESIDENCE TIME - 0.6 SEC.
 MG. LIQUID COLLECTED - 5.2
 MG. STRAIGHT TUBE LOSS - 7.8
 MG OF PYRIDINE SOLUBLE - 2.1
 G.C. CALIBRATION 13296534 COUNTS/MG. C
 TOTAL LIQUID AREA 11910 COUNTS
 TOTAL LIQ. C CONTENT - 1.500 MG
 TOTAL % C IN LIQUID - 10.500

% OF C IN INDIVIDUAL SPECIES

	% IN LIQ.	%C CONVERSION
BENZENE	38.100	4.000
TOLUENE	33.100	3.475
UNKNOWN 5	0.9000	0.094
ETHYLBENZENE	1.300	0.136
O-XYLENE	0.400	0.043
ETHYL-METHYLBENZENE	0.600	0.063
METHYL-PROPYL-BENZENE	0.800	0.058
UN 9	0.000	0.000
TETRALIN:	0.000	0.000
NAPHTHALENE	13.700	1.438
UN 7	0.000	0.000
UN 8	0.000	0.000
2-METHYL-NAPHTHALENE	2.000	0.210
1-METHYL-NAPHTHALENE	0.700	0.073
DIPHENYL	0.500	0.053
UN 6	0.000	0.000
DIMETHYL NAPHTHALENE	0.000	0.000
UN 3	0.400	0.042
ACENAPTHENE	0.000	0.000
FLUORENE	1.700	0.178
1-METHYL-FLUORENE	0.000	0.000
STILBENE	0.000	0.000
UN 4	0.000	0.000
PHENANTHRENE	2.600	0.273
ANTHRACENE	0.000	0.000
UN 1	0.000	0.000
FLUORANTHRENE	0.700	0.073
PYRENE	0.699	0.071
UN 2	0.800	0.084
CHRYSENE	0.500	0.052
3,4-BENZOPYRENE	0.000	0.000
UN?	0.500	0.052

The fractions eluted with pyridine from liquids of several flash hydrogenation runs present a fairly constant yield for reaction temperatures of 650 C to 850 C (Figure 12). A shallow maximum occurs at a reaction temperature of about 800 C.

4.1.2 HPLC Results

A series of runs were conducted using Pittsburgh No.8 and Illinois No. 6 coals. Liquids collected from runs IR76 to IL93 (as described in section 3.2) were eluted with hexane, chloroform, THF with 3% ethanol and pyridine. Each fraction was under evaporation to dryness. The residues were then dissolved in THF to obtain molecular weight distribution curves. Results are summarized in Table 5.

A comparison of molecular weight distribution for flash hydrogenation liquid (PSOC 170 coal at 715 C reaction temperature, 0.6 second vapor residence time, 100 atm hydrogen pre), vacuum pyrolysis liquid (PSOC 170 coal at 465 C , from United Technologies Research Center), Synthoil (from U.S. Bureau of Mines) and tar sands (from Athabasca ARII, W. Seitzer, Sunoco) by steric exclusion chromatography is shown in Figure 13.

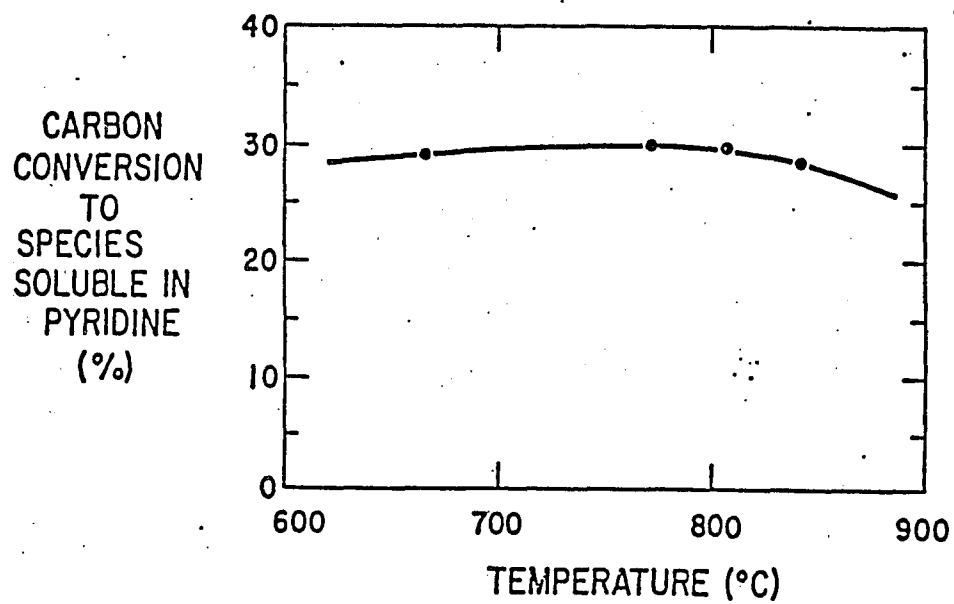


Figure 12 Carbon Conversion to Species Heavier than xylene, insoluble in chloroform and soluble in Pyridine. Pittsburgh No. 8 coal, 100 atmospheres, hydrogen, 0.6 second vapor residence time, 10 seconds contact time, heating rate 650°C per second.

Table 5 Summary of the MW Distribution Data

Run ID	Run T c	<u>Hexane Fraction</u>		<u>CHCl₃ Fraction</u>		<u>THF Fraction</u>	
		Wt. (mg)	Typical MW	Wt. (mg)	Typical MW	Wt. (mg)	Typical MW
IR76	621	0.1	118,138, 197, 463,715	0.9	128,228,430,550	8.6	112,142,190,220, 262,370,443
IL77	643	2.0	127,138	1.5	154,260,380,485	3.0	230, 1140
IL78	668	0.4	123,480	0.8	122,250,483	1.3	176,400,590,970, 1750
IR79	694	0.5	120,169,230, 275	0.6	123,240,425	0.5	190,1000
IR84	685	0.3	118	0.4	132,254	0.6	192,940
IR80	713	1.2	123,133	1.0	326,485	17.9	970,1040
IL85	737	0.3	104	0.5	170,270	2.3	960,1700
IL81	757	0.2	112,123	0.6	115,223,466	11.0	1780,15,000
IR82	781	0.3	219,435	0.2	100,195,435	6.2	1085,15,000
IL86	803	0.3	104,178,212, 262	0.3	123,269	2.7	215,1100
IL87	808	0.7	210	0.2	190	1.6	530,740
IR89	846	0.1	215	0.2	116,215,480	0.3	170,410,750
IL88	964	0.3	215	0.1	470	0.2	215
IR90	897	0.1	118,172	0.3	210	4.9	212,2300
IR92	556	0.1	118	0.5	280,440	3.7	78,220
IL91	682	0.1	112	0.3	128,253,460	2.3	223,970,2200
IL93	504	0.1	120	1.3	300,470,820	3.5	215,780

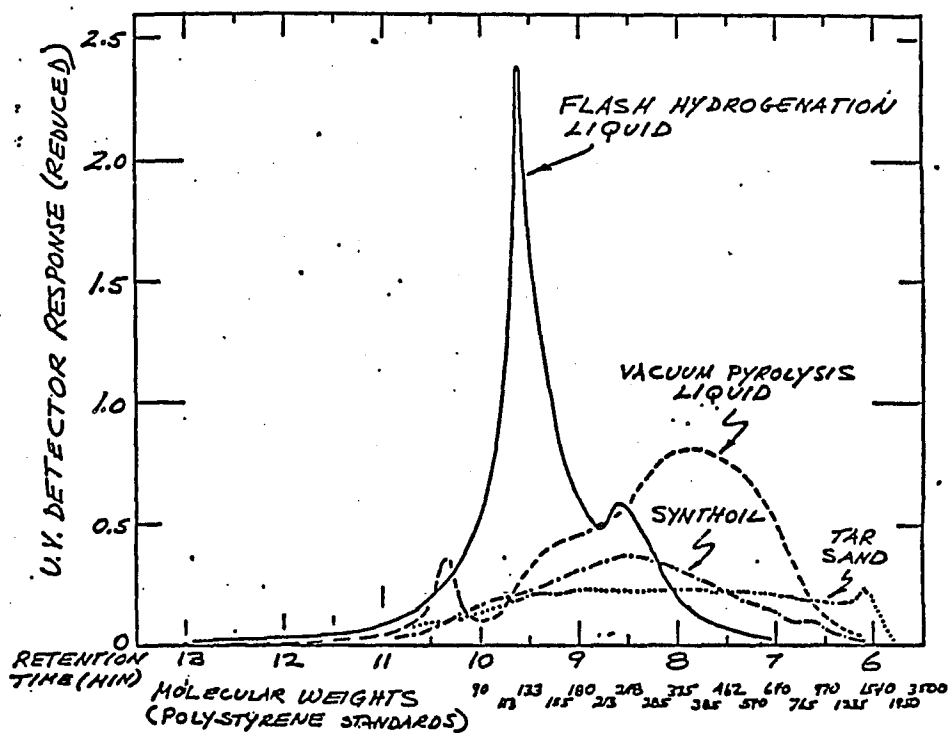


Figure 13 Molecular Weight Distribution of Illustrative Synthetic Liquids.

Flash Hydrogenation Liquid: from PSOC 170 coal at 715°C, 0.6 sec. v.r.t., 100 atm. H₂, The City College.

Vacuum Pyrolysis Liquid: from PSOC 170 coal at 465°C, P. Solomon, United Technologies Research Center.

Synthoils: U.S. Bureau of Mines.

Tar Sand: Athabasca ARII, W. Seitzer, Sunoco.

In this graph the molecular weight of flash hydrogenation liquid is as high as about 640, for vacuum pyrolysis liquid and synthoil about the 1500 range, and for tar sands more than 2000. The flash hydrogenation liquids and vacuum pyrolysis liquids have bimodal distribution curves; synthoil and tar sands have single broad peaks. Although the quality of the liquids changes with operating conditions for the same coal, it is still interesting to note that a high proportion of the flash hydrogenation liquid has a molecular size below 180. Most vacuum pyrolysis liquid is between 180 and 600.

A steric exclusion liquid chromatography column fractionates the samples according to molecular size and not to molecular weight. To relate the retention times of the fractions to their molecular weight, it is necessary to calibrate the column with compounds of similar structure to those present in the sample. However, these are not readily available for coal derived liquids, since there are many different types of coal liquid structure, depending upon the nature of the coal and the treatment. Also, in this case, samples were too small to use vapor pressure osmometry (VPO) to measure their molecular weight.

In the present research, calibrations were performed daily using polystyrene standards and several aromatic and polycyclic aromatic hydrocarbons. Therefore, the actual

molecular weight distribution may differ from the one obtained here and the results should be interpreted with some caution.

4.2 COMPARISON OF HYDROGENATION BEHAVIOR OF TWO BITUMINOUS COAL

4.2.1 Experimental Results

Illinois No.6 coal (sample A) and Pittsburgh No.8 (Ireland mine) coal were used in this study comparing the hydrogenation behavior of two bituminous coal. Both the elemental and the proximate analysis of these two coals are presented in Table 6.

In the following, data for Illinois No. 6 coal were published previously (Dobner et al. 1976). Curves representing these data are shown together with data points for Pittsburgh No. 8 coal for comparison.

Figure 14 shows the carbon conversion to methane in both coals as a function of the temperature. Yields of methane from Illinois No. 6 coal are slightly higher at the same reaction conditions.

ANALYSIS OF COALS

PROXIMATE ANALYSIS

	<u>Illinois #6 Coal</u>		<u>Ireland Mine Coal</u>	
	<u>As Received</u>	<u>Dry Basis</u>	<u>As Received</u>	<u>Dry Basis</u>
Moisture	3.30		1.25	
Volatile	39.10	40.44	39.85	40.35
Fixed Carbon	45.25	46.79	46.30	46.89
Ash	12.35	12.77	12.60	12.76
B.T.U.	11,464	11,855	12,665	12,825
Pyritic Sulphur	0.15	0.16	2.18	2.21
Organic Sulphur	3.00	3.10	3.43	3.47
Sulphate Sulphur	0.04	0.04	0.04	0.04

ULTIMATE ANALYSIS

Moisture	3.30		1.25	
Carbon	64.11	66.30	68.73	69.60
Hydrogen	4.82	4.98	4.85	4.91
Oxygen	11.11	11.49	5.73	5.80
Nitrogen	1.12	1.16	1.19	1.21
Sulphur	3.19	3.30	5.65	5.72
Ash	12.35	12.77	12.60	12.76

Table 6

Proximate and ultimate analysis
of the coals used during this
research

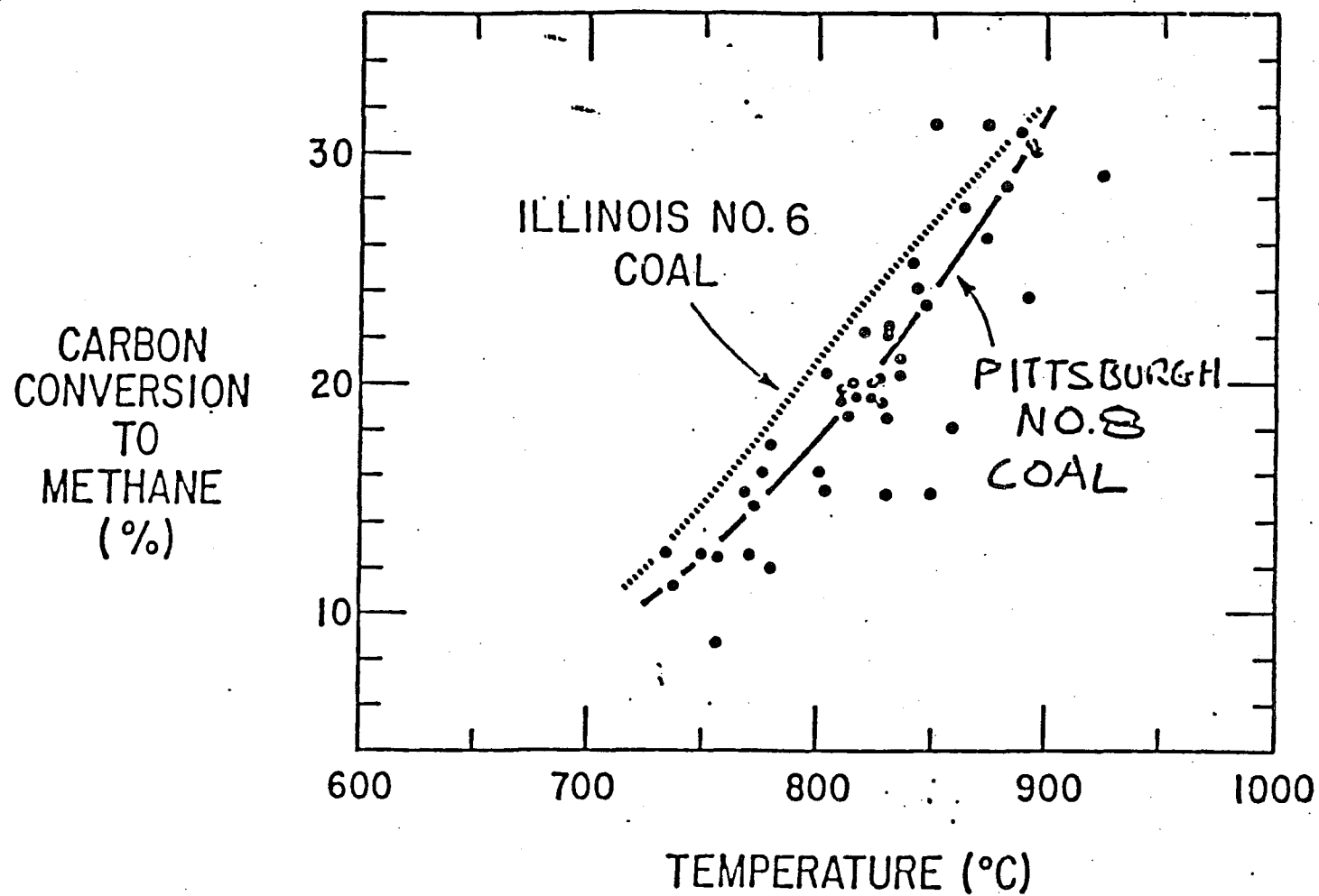


Figure 14 Carbon conversion to methane, showing slightly higher yields for Illinois No. 6 coal.

In Figure 15 carbon conversions to ethane and propane are presented. While conversions to propane do not show much of a difference, the temperature at which the maximum yield of ethane obtained is higher for Pittsburgh No. 8 coal.

Carbon conversions to BTX are shown in Figure 16. Although the data scatter considerably, the maximum yield of BTX attainable from Pittsburgh No. 8 coal is lower (about 2 % less). Also, the maximum appears at a higher temperature in this coal.

Figure 17 shows the differences of behavior between these coals - the yields of liquids heavier than BTX appear as a function of temperature. While for Illinois No.6 coal the yield of heavy materials decays rapidly with temperature, for Pittsburgh No. 8 coal the yield has a maximum at about 650 c followed by a decay at higher temperatures.

Table 7 shows a typical characterization of fractions obtained by our modified SESC procedure. It includes the molecular weight distribution of each liquid fraction from both Illinois No. 6 and Pittsburgh No. 8 coals. Tentative chemical structures are also assigned. The structural assignments are based, for fractions 1 and 2, on NMR analysis of our samples at City College, and for the remaining fractions by comparison with the results reported by Farcasiu (1977) in the SESC separation of several coal derived liquids.

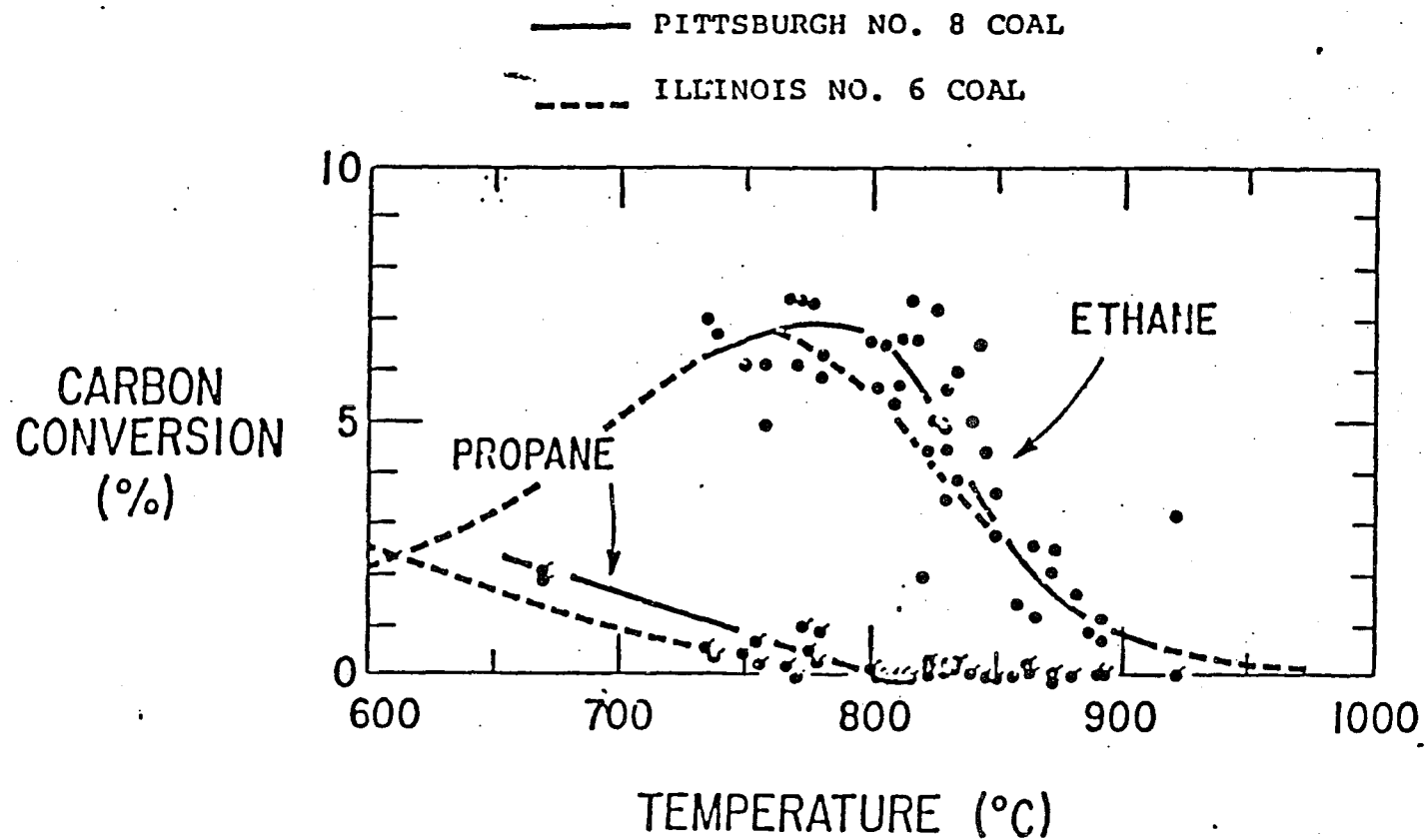


Figure 15 Carbon conversion to propane and ethane. The maximum yield of ethane is observed at higher temperatures in Pittsburgh No. 8 Coal.

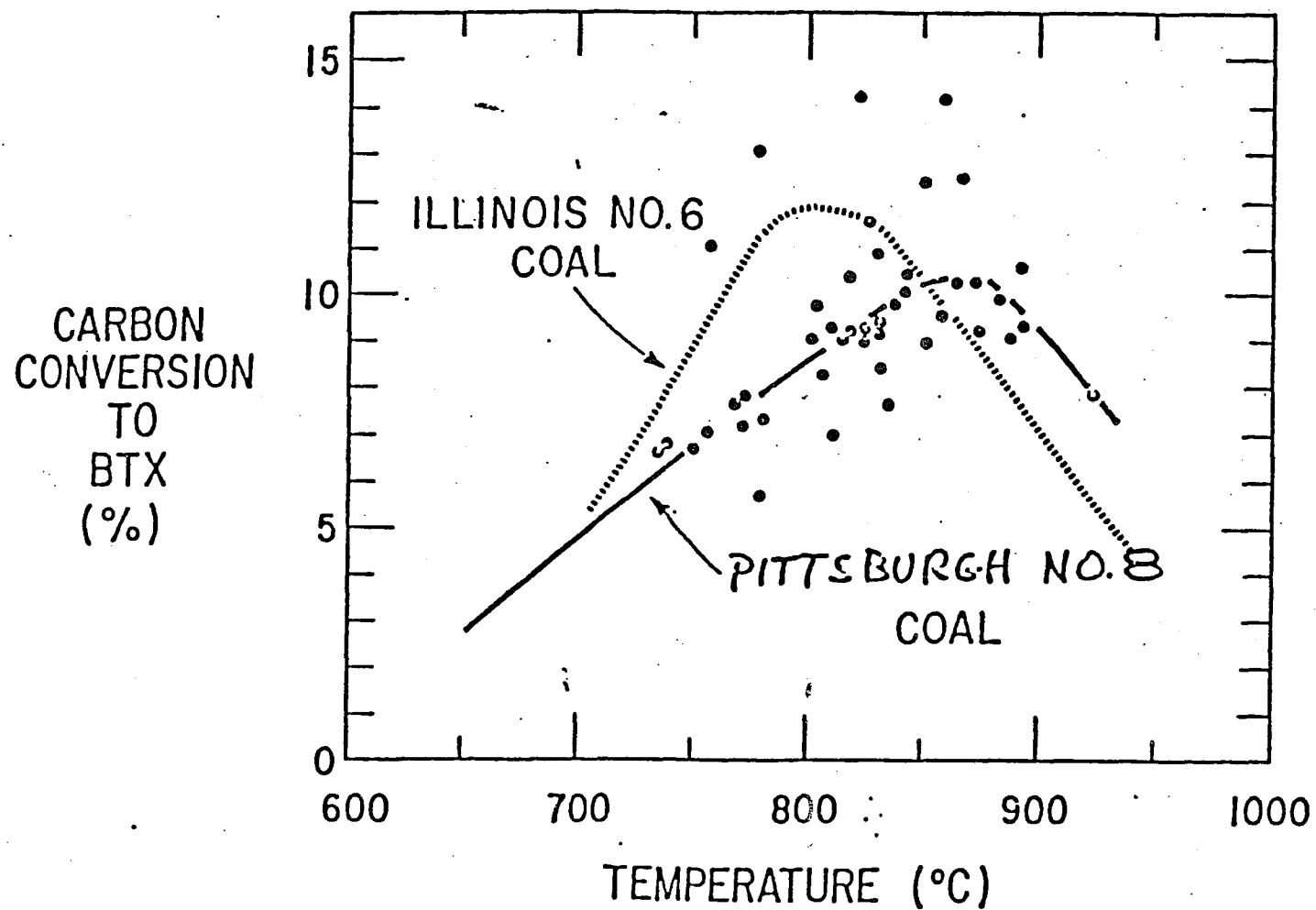


Figure 16

Carbon conversion to BTX. The maximum yield of BTX is obtained at higher temperatures in Pittsburgh No. 8 Coal.

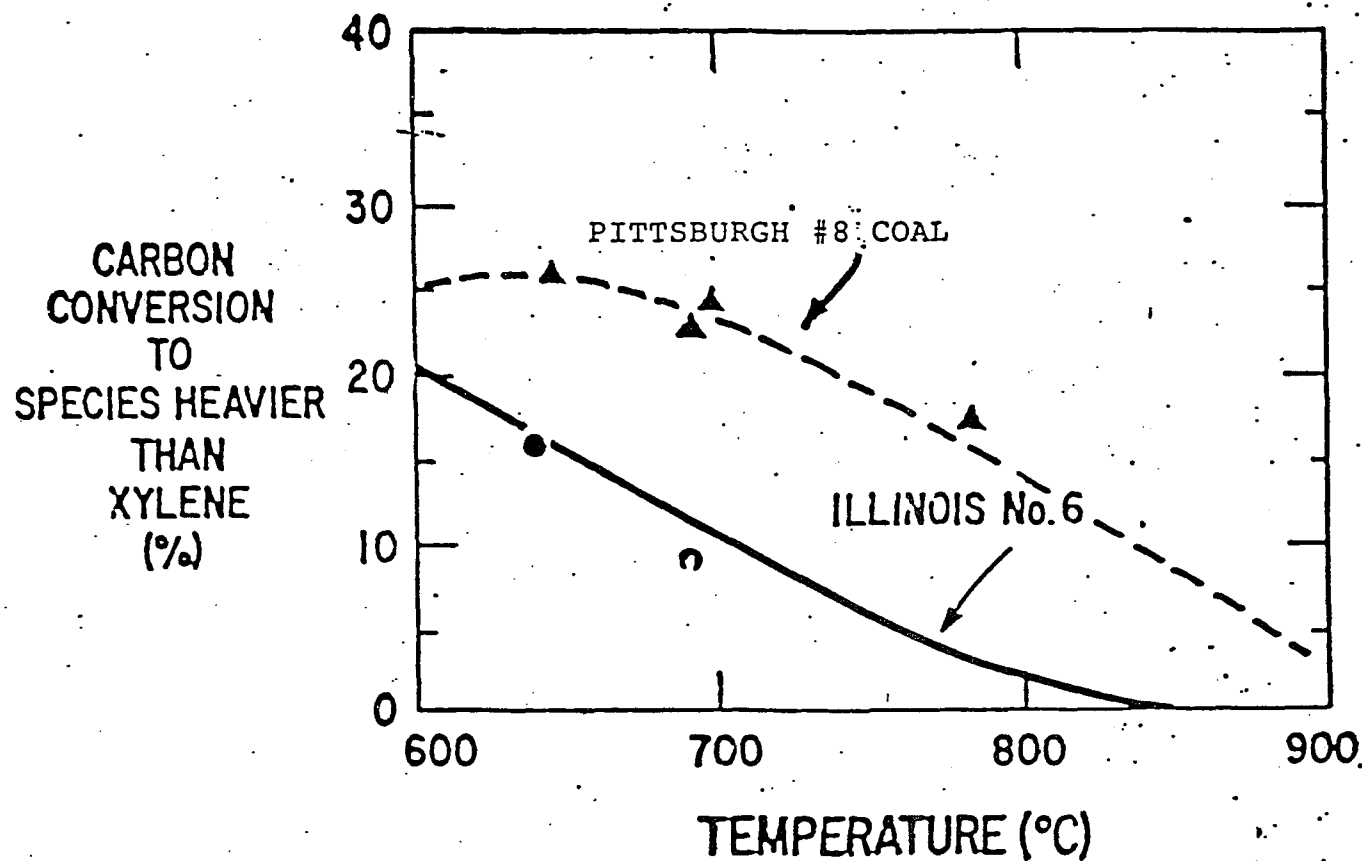


Figure 17 Carbon conversion to species heavier than xylene. Species decay rapidly with temperature in Illinois No. 6, but present a maximum and decay at higher temperatures in Ireland Mine Coal

TABLE 7. CHARACTERIZATION OF SESC FRACTIONS

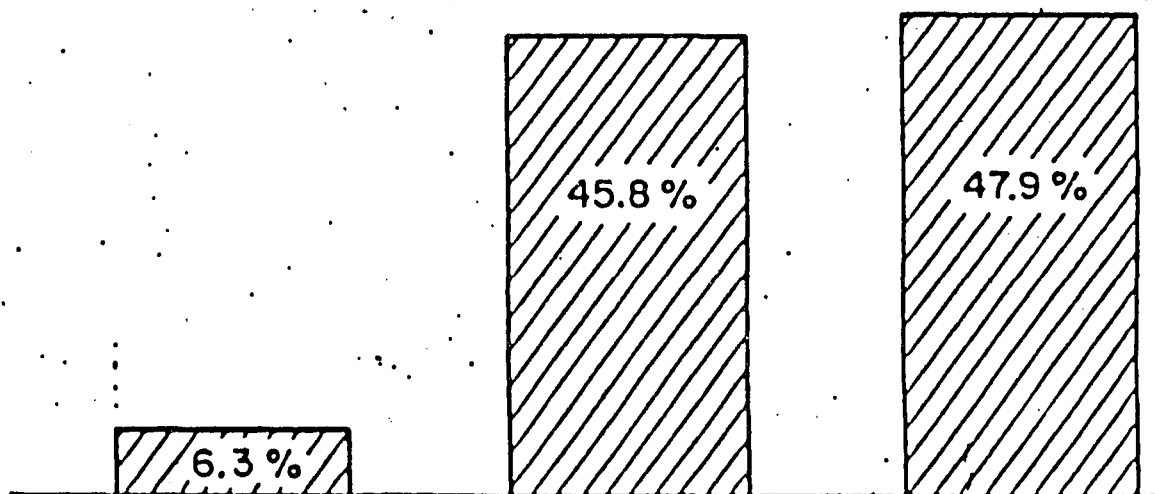
<u>Fraction</u>	<u>Solvent Eluent</u>	<u>Chemical Structure (Possible)</u>	<u>Molecular Weight (Steric Exclusion Chromatography)</u>	
			<u>Pitts. No. 8 coal</u>	<u>Ill. No. 6 coal</u>
1.	Hexane	Aromatics, Alkyl-Aromatics. (N.M.R.)	200	245
2	Chloroform	Aromatics, Polar Aromatics with - H and - Cl ₃ Groups (N.M.R.)	310	465
3	Ether/3:1 EtOH	Monophenols, Basic N Heterocyclics (Farcasiu, 1977)	440	460
4	Methanol	Highly Functional Molecules, High Heteroatoms Content (Farcasiu, 1977)	435	425
5	Chloroform/ 3:1 EtOH	Polyphenols; (Farcasiu, 1977)	640	640
6	THF	Increased O, Increased N, Basicity (Farcasiu, 1977)	975	---

Molecular weight distribution of the SESC fractions of heavy liquids from both coals. Steric Exclusion Chromatography results show the molecular weight at the peak, accordingly to a calibration of the column with polycyclic aromatics and polystyrene standards.

Molecular weight, it may be noted, increases as fraction number increases. These results will be discussed in more detail later.

Table 7 gives an account of the molecular weight distribution of each fraction and shows assignments of possible chemical structures. With regard to molecular weight, it may be noted that these are about the same in the various fractions (except in fraction 2) for these two coals. Figure 18 shows the weight percent conversion of liquids heavier than BTX where "oils" correspond to fractions eluted with hexane and chloroform, "asphaltenes" are fractions eluted with ether/ 3% ethanol and "multi-functionals" are fractions eluted with methanol, chloroform and THF. Table 8 gives a detailed comparison of the product distribution from the two coals at similar conditions also shown in figure 19. The yield of gases is approximately the same; the difference is more marked in the liquid fractions. Coal flash hydrogenation products from Pittsburgh No. 8 contain a large fraction of "asphaltenes" and "multifunctional" liquids. These differences, since the reaction conditions are almost the same, must arise from differences in the chemical structure of the coals themselves.

PITTSBURGH NO.8
COAL



ILLINOIS NO.6
COAL

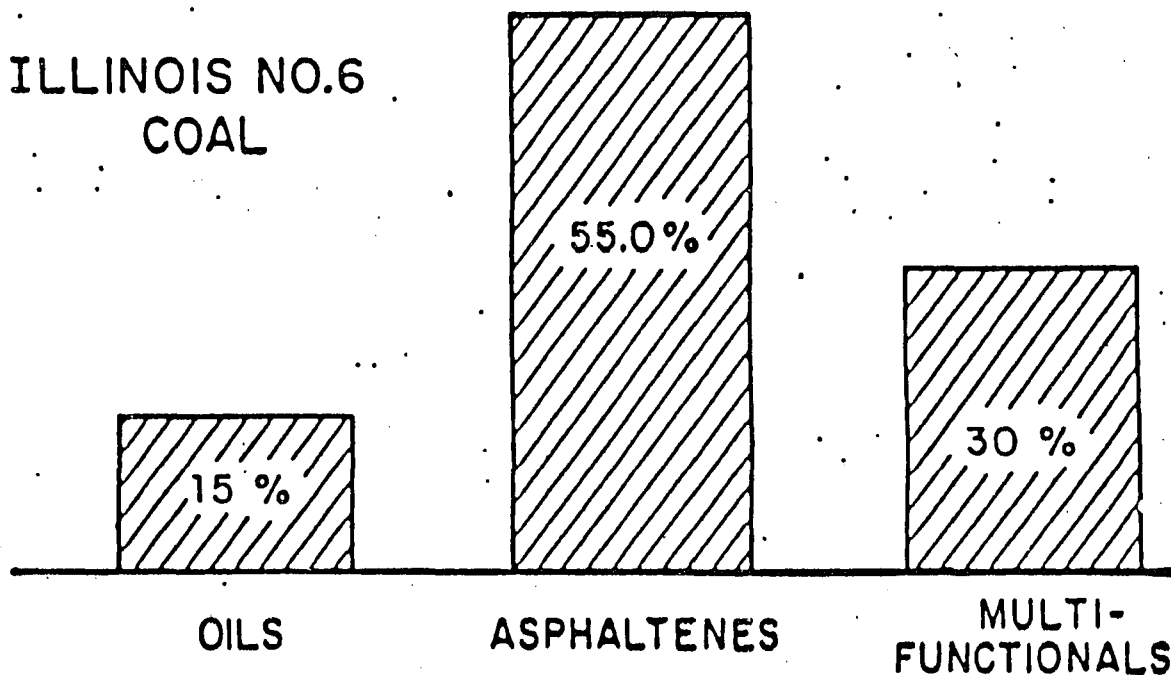


Figure 18 Comparison of SESC Analyses for Heavy Liquids
from Two Bituminous Coals

TABLE 8 COMPARISON OF PRODUCTS DISTRIBUTION FROM PITTSBURGH
NO. 8 COALS AND ILLINOIS NO. 6 COALS

	<u>% Carbon Conversion to Products</u>	
	<u>Pitts. No. 8</u> <u>685 C</u>	<u>Ill. No. 6</u> <u>678 C</u>
Methane	6.0%	8.0%
Ethane	5.0%	5.0%
Propane	2.0%	1.5%
CO _x	2.7%	3.7%
BTX	4.5%	4.5%
Oils	1.4%	1.14%
Asphaltenes	10.2%	4.15%
Multifunctionals	10.67%	2.26%
Char	58.0%	65.0%
Total	100.47%	95.25%
Total gases and liquid conversion (by differ- ence)	42.0%	35.0%
Maximum Conversion	60.0% (at 820 C)	45.0% (at 800 C)

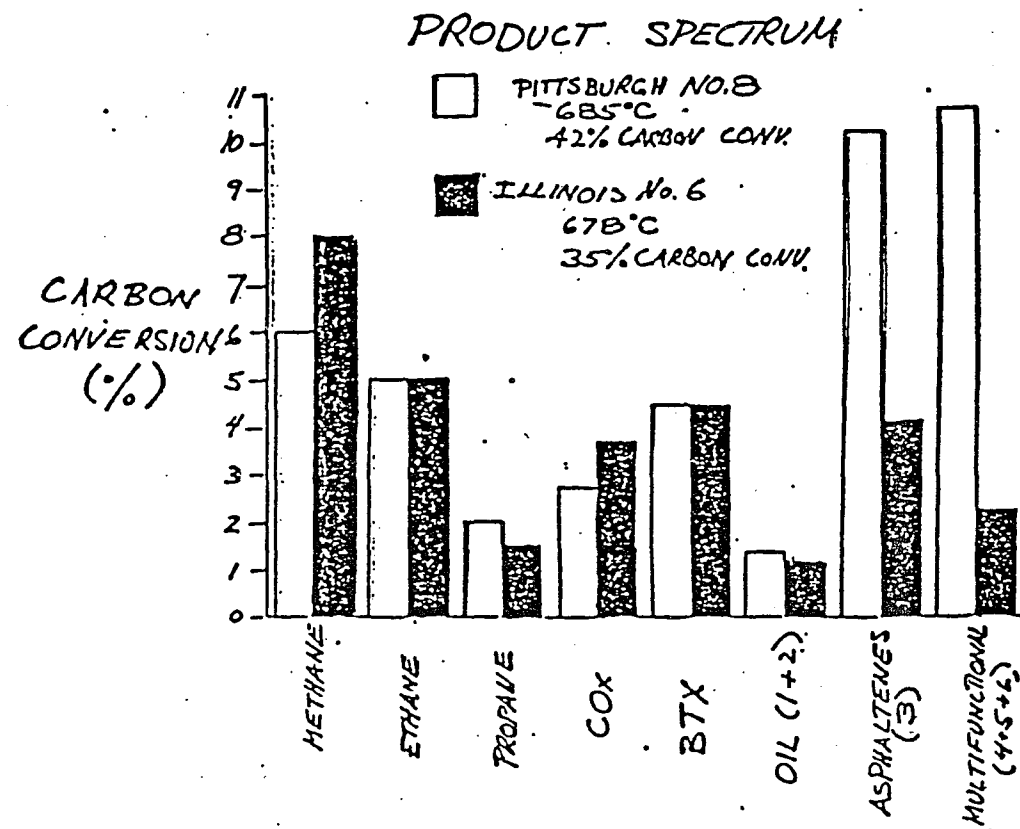


Figure 19

Comparison of the modified SESC analysis of the liquids heavier than BTX obtained in flash hydrogenation of two bituminous coals.

4.2.2 Modeling Of Flash Hydrogenation Reaction

Although several models have been proposed, as outlined in a review by Anthony and Howard (1976), the complex pyrolysis and hydropyrolysis behavior of coal is not well understood yet. In order to compare in more detail our results on hydrogenation of Illinois No. 6 coal and Pittsburgh No. 8 coal, the following model is proposed.

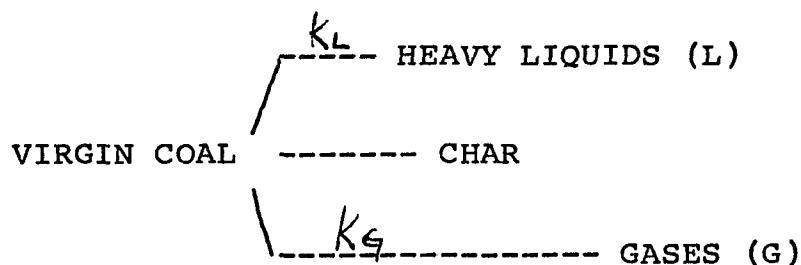
A modified coal devolatilization model based on first order kinetics proposed by Solomon and Colket (1978) was first used. This model contained a set of structural parameters which are the initial content of chemical functional groups. However, there is disagreement between experimental data and the model predictions for both coals. From Wei and Prater (1962), the yield of each component for first order kinetic models under fixed reaction conditions can be expressed as a linear combination of the initial compositions. Thereafter, a simple model was developed as follows.

Flash hydrogenation reactions are assumed to take place in two stages: a pyrolysis, in the presence of hydrogen, of the coal to yield primary heavy liquids and gases (solid phase reaction), and further thermal hydrocracking reactions of these liquids to single ring aromatics and more gases (gas phase reaction). Single ring aromatics are also assumed to hydrocrack to gases. The reactions of carbon deposition from the liquids are neglected.

The pyrolysis of the coal is assumed to follow first order kinetics controlled by the temperature of the solid and the solid reaction time. Pressure effects are not considered in this model since all data were obtained at constant pressure (100 atm). Diffusional effects are assumed to be included in the kinetic constants. Volatiles are lumped into three components: gases (methane, ethane, propane and carbon oxides), heavy liquids (compounds that are heavier than xylene) and BTX (benzene, toluene and xylene).

Pyrolysis is followed by reactions in the gas phase which are controlled by vapor temperature and residence time. BTX is assumed to appear primarily through the hydrocracking of heavy liquids in the vapor phase, following experimental evidence from this laboratory.

The primary pyrolysis of coal is described by the reactions:



and the rates of generation of product species given by:

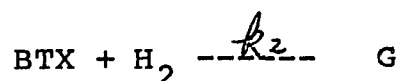
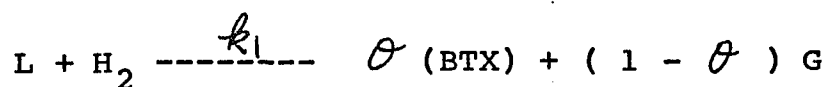
$$dL/dt_s = k_L (L^* - L)$$

$$L(0) = 0.$$

$$dG/dt_s = k_G (G^* - G)$$

$$G(0) = 0.$$

The vapor phase thermal hydrocracking reactions are:



where θ is the mass fraction of liquid that can be hydrocracked to give BTX. L^* and G^* are the fraction of the initial carbon in the coal that can be transformed to heavy liquids or gases, k_G and k_L are the first order kinetic constants in the formation of heavy liquids and gases during hydropyrolysis, and k_1 and k_2 are the kinetic constants of the thermal hydrocracking in the vapor phase.

This model can be solved analytically for isothermal conditions (see figure 20). From previous experiments (Dobner et. al. 1977) it is known that

$$K_2 = 8.76 \times 10^9 \text{ EXP } (-52,400./RT)$$

For solid phase reactions:

The rate of gas and heavy liquids production are given by:

$$\frac{dG}{dt} = K_G (G^* - G)$$

$$\frac{dL}{dt} = K_L (L^* - L)$$

the above equations may be *analytically* integrated to give:

$$-\ln \frac{G^* - G}{G^*} = K_G t$$

hence, $G^* - G = G^* e^{-K_G t}$

Therefore, $G = G^* (1 - e^{-K_G t})$

and $L = L^* (1 - e^{-K_G t})$

For vapor phase reactions:

The rate of liquids consumption is:

$$dL/d\tau = -K_1 L$$

hence, $L = L_0 e^{-K_1 \tau}$

and the rate of gases and BTX production are:

$$\frac{dBTX}{d\tau} = \theta K_1 L - K_2 BTX$$

$$\frac{dG}{d\tau} = (1 - \theta) K_1 L + K_2 BTX$$

Therefore, total heavy liquids is $L = L^* (1 - e^{-K_L t}) e^{-K_1 \tau}$

Figure 20 - Model Equations for Flash Hydrogenation

A nonlinear parameter estimation technique was used to find the kinetic parameters of the model for each coal. The Powell method, from a standard subroutine package (IMSL), was used. The computer program is listed in Appendix I. The data set used to find the parameters contained 16 data points (with 4 components each) obtained from flash hydrogenation runs with Illinois No. 6 coal and 40 points obtained from runs with Pittsburgh No. 8 coal. All the data were obtained from experiments performed under 100 atm. of hydrogen pressure, 0.6 seconds vapor residence time, and 10 seconds of solid contact time. Yields were expressed as percentage of the initial carbon present in the coal. The parameters obtained from the regression procedure are presented in table 9.

The distribution of products as a function of the temperature at fixed solid and vapor residence times (as described by the model) is presented in Figure 21 compared with the experimental data for Pittsburgh No. 8 coal. The average standard deviation of the experimental results with respect to the values given by the model is 5.44%, the same order of magnitude as the standard deviation of the experiments. The definition of the standard deviation used here is the square root of the sum of difference squares between calculated value and experimental data divided by the absolute value of four times the number of data points.

**TABLE 9 KINETIC PARAMETERS OBTAINED FROM
EXPERIMENTAL DATA AND REGRESSION PROCEDURE**

	<u>Illinois No.6 Coal</u>	<u>Pittsburgh No.8 Coal</u>
G^*	0.2576	0.2484
L^*	0.2854	0.3383
k_{GO}	1.676	49.91
E_G	6542.0	12030.0
k_{LO}	5.424	52.15
E_L	6110.0	10010.0
k_{10}	1.6×10^6	4.51×10^4
E_1	28180.0	21810.0
θ	0.5460	0.5691

VALUES OF THE KINETIC CONSTANTS OF THE MODEL AT 800 C

	<u>Illinois No.6 Coal</u>	<u>Pittsburgh No.8 Coal</u>
k_G	0.0795	0.1835
k_L	0.3146	0.4915
k_1	3.17	1.73

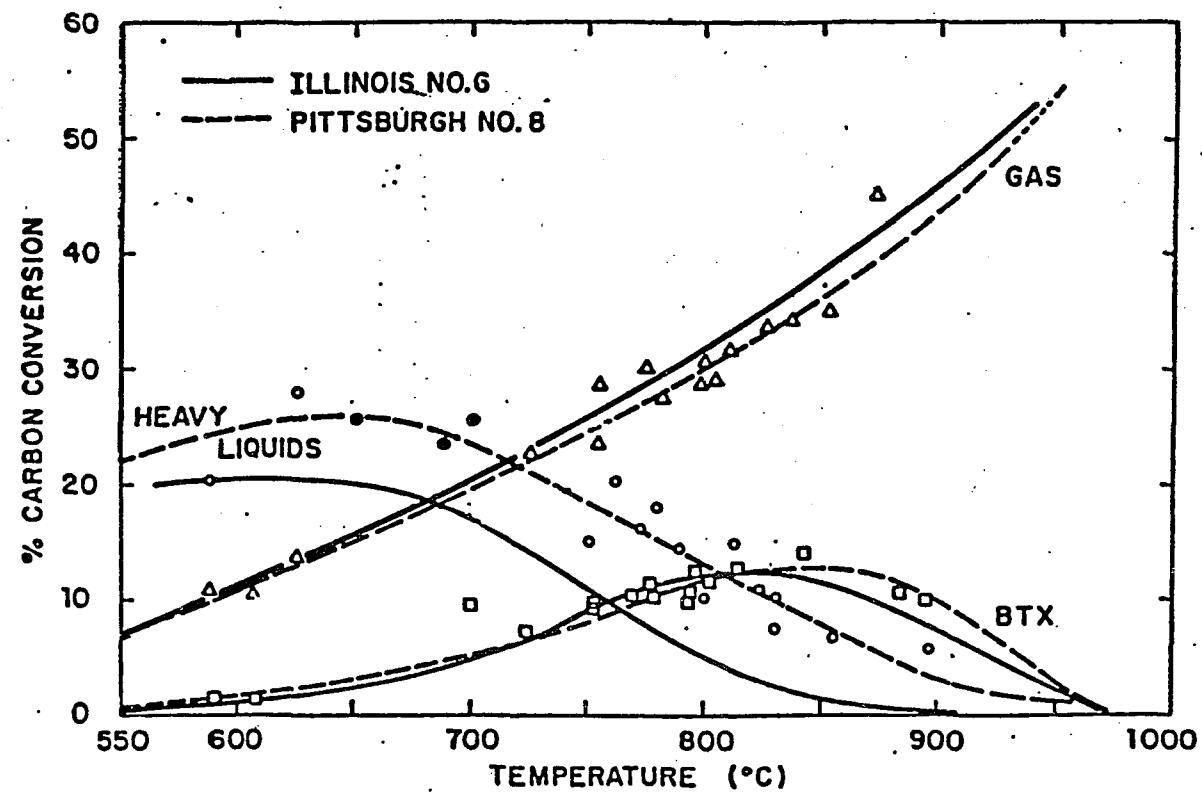


Figure 21: Modeling of Flash Hydrogenation. Lines are model results. Points are experimental data for Pittsburgh No. 8 coal: Δ gas, $\circ$ heavy liquids by carbon balance, $\bullet$ heavy liquids by collection, $\square$ BTX.

From the calculated values of L^* the fraction that can be converted to heavy liquids is higher in Pittsburgh No. 8 coal. The value of G^* for both coals is about the same, so that the model suggests that the differences in gas yields come about by the secondary reactions of gas production.

Another feature of the model is that the calculated energies of activation in the pyrolysis step are higher in Pittsburgh No. 8 coal. In all cases, the activation energies are smaller than what would be expected from elementary chemical steps. It may reflect transport limitation or the disadvantages of a simplified first order model. Since when a first order reaction is assumed in coal pyrolysis modeling, the actually different reactions in different temperature intervals have to be balanced to fit the overall temperature dependence, hence the activation energy and the pre-exponential factor have to be very low. Therefore a more complex sequence of events for the coal pyrolysis is suspected.

From the results given in Table 9, it may be observed that the kinetic constants for the same steps are of the same order or magnitude for both coals. However, at 800 C the rate of gas and liquid formation during pyrolysis is higher in Pittsburgh No. 8 coal, but the rate of decomposition of the heavy liquids to BTX and gas is higher in the Illinois No.6 coal.

4.2.3 Discussion

A comparison of yield distributions from the flash hydrogenation of two bituminous coals reveals several differences. Illinois No.6 coal tends to give more methane and carbon oxides than Pittsburgh No. 8 coal, while conversely, Pittsburgh No. 8 coal tends to give higher yields of liquids.

Higher carbon oxides yields can be expected, since Illinois No.6 coal contains more oxygen, and oxygen content in coals has been shown to correlate positively with yields of carbon oxides (Chen et al., 1983).

Higher methane yields in Illinois No.6 coal are more difficult to explain from a coal-structure point of view. An analysis of both coals by Fourier Transform Infrared spectroscopy reveals that both coals have an identical 3.3% of aliphatic hydrogen so that the difference in methane yields cannot be attributed to strong differences in the amount of aliphatic groups present initially in the coal structure. The only factor that could explain such differences in methane yield is the higher sulphur content of Pittsburgh No. 8 coal. From Graff et al. (1980) in coals there is a negative effect of sulphur on methane yields. However, this effect would account for only part of the difference.

Similarly, the yields of total liquids (BTX and heavy liquids) are higher in Pittsburgh No. 8 coal, and this is again difficult to explain with our limited knowledge of these coals.

It was shown that there is a strong correlation between liquid yields in pyrolysis of coal and the content of aliphatic hydrogen in the coal; the correlation holds in flash hydropyrolysis and in liquefaction (Graff et al. 1980).

However, in the present case, both coals have identical contents of aliphatic hydrogen, so that these differences are not predicted by that correlation. From Graff et al. (1980) the total liquid yields were found to increase with carbon content. In the present case, Pittsburgh No. 8 coal has a slightly higher carbon content. Using that correlation it can be shown that this slight difference in rank can account for at least part of the difference in total liquid yields. The remainder of the difference is still unexplained.

Another unexpected result shown by the experiments is that Pittsburgh No. 8 coal gives a higher yield of total volatiles in flash hydrogenation. The correlation based on aliphatic hydrogen and oxygen from Graff et. al. (1980) predicts the opposite. The exinite content may be significant in the total yields from hydropyrolysis, but

this correlation could not be verified here due to the lack of knowledge of maceral content.

Compounds that exhibit a maximum as a function of temperature, such as ethane and BTX, also behave differently in the two coals. The peaks for both compounds in the case of Pittsburgh No. 8 coal has the maximum at higher temperatures. From the kinetic point of view the shifting of the maximum can be due to a lower rate of formation of an intermediate compound. In the case of BTX the model developed tends to confirm this idea, since the kinetic constant for liquid decomposition (or BTX formation) is lower for Pittsburgh No. 8 coal. This difference in the kinetics of heavy liquids decomposition suggests a difference in structure of liquids from the two coals.

The curves of heavy liquid yields as a function of temperature also show a similar difference. Heavy liquid yields from Pittsburgh No. 8 coal have a maximum at 650 C and decay at higher temperatures. In the case of Illinois No.6 coal, heavy liquid yields do not have a maximum in the range of this experimental study, but decay continuously. As a result, yields of heavy liquids from Pittsburgh No. 8 coal are higher over the entire temperature range studied.

From the modeling study (Table 9) it is suggested that the activation energy for liquid formation is higher in the case of Pittsburgh No. 8 coal. This would explain the

shifting of the maximum toward higher temperatures, and would also suggest a slightly different mechanism of heavy molecule detachment in each case.

The study of heavy liquids composition by modified SESC and steric exclusion shows very interesting differences. Both the average and the molecular weight of individual fractions in modified SESC separation have approximately the same molecular weight. This fact is surprising since it would be expected that one of the coals would give a "heavier" liquid representative of a larger average molecular domain in the coal.

From the results of heavy liquids analysis and from the modeling study, it is apparent that Pittsburgh No. 8 coal gives a higher heavy liquids yield during the reaction. The model suggests that the fraction of liquid yielding coal (L*) is higher in Pittsburgh No. 8 coal.

The modified SESC analysis of the heavy liquids for both coals indicates a marked difference in their nature (Figure 18). Illinois No.6 coal liquids tend to have lower proportions of nonpolar oils and polar multifunctional molecules. Pittsburgh No. 8 coal liquids have higher fractions of oils and polyfunctionals. The net difference then is that the heavy liquids of Pittsburgh No. 8 coal have a higher fraction of heteroatoms and polar polyfunctions. Although these coals behave similarly with respect to the

production of gases and BTX, there are marked differences that have to be discussed further.

The heavy liquid fraction produced by Illinois No.6 coal tends to disappear rapidly with increased temperature. This behavior can be explained by cracking and hydrocracking reactions occurring in the coal and in the vapor phase producing char, BTX and gases.

Pittsburgh No. 8 coal produces a heavy liquid fraction that starts disappearing only at higher temperatures. This behavior indicates that these liquids are more refractory than those of Illinois No.6 coal. As a result, less char is produced and the maximum yields of BTX and ethane (products of the hydrocracking reaction) are obtained at higher temperatures.

From the modified SESC and steric exclusion analyses of the heavier liquid fractions we arrive at an explanation for this difference in reactivity. From Figure 16 it is clear that liquids from Pittsburgh No. 8 coal contain proportionately more liquid products. The net result is a higher proportion of heteroatoms and polyfunctionals. These are assumed to be more difficult to break down in the thermal hydrocracking of these fractions to BTX.

It is possible to assume that the coals have different chemical structure. One important difference is that the

oxygen content of Illinois No.6 coal is almost double that of Pittsburgh No. 8 coal. Oxygen and aliphatic hydrogen are important factors in determining the reactivity of a coal. Since the content of aliphatic hydrogen is approximately the same in both coals, it can be argued that the higher oxygen content of Illinois No.6 coal explains the higher oxygen content of the liquids obtained, as well as being responsible for this coal's higher reactivity.

4.3 FLASH STEAM PYROLYSIS LIQUIDS

The coal used in flash hydrolysis studies was Illinois No. 6 coal, using about 100 mg for each run. The solid residence time was 2 minutes and the vapor residence time was 0.2 seconds. Coal was pyrolyzed in steam at pressures which varied from 660 to 750 psia by flash heating to temperatures from 513 to 746 C. The liquids were collected and weighted as described in section 3.3. Each sample was further analyzed to get the molecular size distribution and the elemental compositions by the methods described previously. The yields and elemental analysis of flash hydrolysis liquids are presented in table 10. The percentages of carbon, hydrogen, and nitrogen of each sample were also corrected to an ash-free basis. The percentage of

oxygen plus sulfur was determined by difference. The elemental compositions of those liquids obtained at 700 psia of steam are plotted vs. reaction temperature and presented in figure 22.

Molecular Weight Distribution

The collected flash hydrolysis liquids were analyzed, with THF used as a solvent. The molecular weight distribution of most liquids appeared to be bimodal with maxima in the range of MW 125 to 250. The values for number-average molecular weight and weight-average molecular weight of the liquids (Table 11) were obtained from the following equations (Schanne and Haemel, 1981) :

$$M_n = \frac{\sum_{i=1}^n H_i}{\sum_{i=1}^n \frac{H_i}{M_i}}$$

$$M_w = \frac{\sum_{i=1}^n H_i M_i}{\sum_{i=1}^n H_i}$$

where : H_i , peak height of molecular species i ; M_i , molecular weight obtained from the calibration plot; M_w , weight-average molecular weight; M_n , number-average molecular weight.

A simulated boiling point distribution curve was obtained for run P36 on 3% Dexil GC column (Fig. 23).

Table 10

Yields and Elemental Analysis of Flash Hydrolysis Liquids

Run No	Pressure (psi)	Temp (°C)	Yield of Liquids (%)	Composition of Liquids				Carbon Conversion of Liquids** (%)
				C%	H%	N%	Ash*%	
P 33	660	627	5.89	71.69	5.40	1.25	5.76	6.26
P 29	700	551	10.47	64.73	4.99	2.12	14.22	10.03
P 26	700	585	10.68	65.65	6.09	2.03	1.24	10.38
P 35	700	645	6.72	73.85	6.10	1.13	2.22	7.34
P 34	700	696	9.98	64.33	6.60	0.84	2.05	9.50
P 14	700	723	12.45	54.10	7.25	0.70	3.61	9.97
P 2	700	746	9.32	63.43	8.08	0.43	4.23	8.89
P 30	725	513	7.06	72.70	7.72	1.23	1.25	7.59
P 36	750	599	5.77	73.58	7.15	1.06	0.83	6.28

* Ash is inorganic impurities

** Carbon Conversion of Liquids = $\frac{\%C \text{ in liquid} \times \text{wt. of liquid}}{69.1\% \times \text{wt. of coal} \times (1 - \text{moisture})}$

moisture = 2.22%

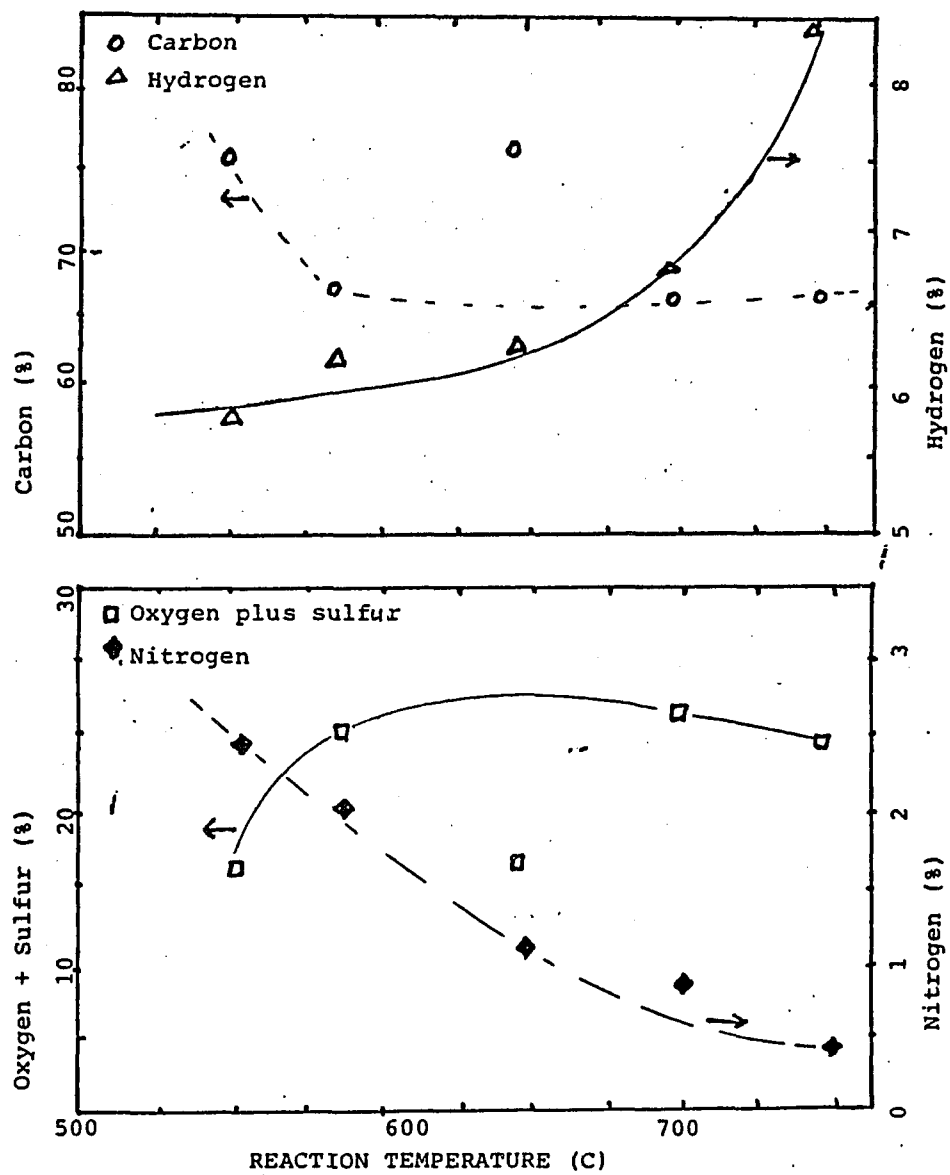


Figure 22 Effect of Reaction Temp. on elemental compositions of flash hydrolysis liquids

Table II Average Molecular Weight of Flash Hydrolysis Liquids

<u>Run No.</u>	<u>Pressure (psi)</u>	<u>Temp (°C)</u>	<u>Mn</u>	<u>Mw</u>
P 33	660	627	173	412
P 29	700	551	172	280
P 26	700	585	216	452
P 35	700	645	151	281
P 34	700	696	172	333
P 2	700	746	199	564
P 30	725	513	178	269
P 36	750	599	163	318

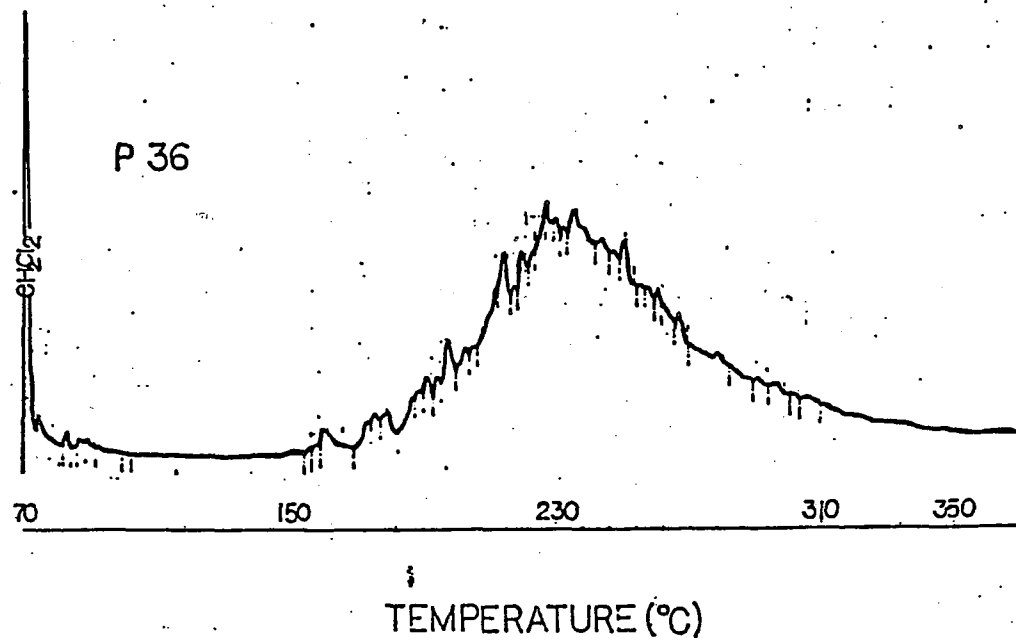


Figure 23 Chromatographic Boiling Point Distribution Curve Obtained on 3% Dexil Column.

Sample P36 prepared at 599 C and 750 psia.

4.4 COMPARASION OF HELIUM/STEAM PYROLYSIS AND HYDROPYROLYSIS

The distribution of products from coal pyrolysis in hydrogen, steam/helium mixture, and pure helium as obtained by Cities Service R&D Co. is presented in Table 12. The total yield in hydropyrolysis is higher than in steam pyrolysis, which in turn is much higher than in helium atmosphere pyrolysis under the same operating conditions. The liquid products from hydrogen and steam/helium runs were further analyzed and the results are presented below.

Table 13 gives the elemental composition of liquid products. Table 14 shows the results of the modified SESC fractionation of liquid products and shown as bar graph in Fig. 24. A material balance shows that 86% of the hydrogen run liquids and 88% of the steam/helium liquids have been recovered with some losses, probably a residuum left in the silica gel column. As shown in Table 15 (the elemental analyses of modified SESC fractions), the carbon content of each fraction is decreasing with increasing fraction number. The atomic hydrogen to carbon ratios of modified SESC fractions of both liquids are shown in Table 17.

Table 12 Products Distribution (In % of total conversion)

	<u>Hydrogen run</u>	<u>7.6% Steam in Helium</u>	<u>Helium run</u>
CO _x	1.2	5.2	1.8
CH ₄ -C ₄ H ₈	20.2	7.3	7.5
BTX*	8.2	1.1	1.6
Liquids	9.8	12.1	6.1
Total	39.4	25.7	17.0

(* Analyzed as part of the gaseous products using gas chromatography).

Table 13 ELEMENTAL COMPOSITION OF LIQUID PRODUCTS

<u>SAMPLE</u>	<u>C (Wt.%)</u>	<u>H (Wt.%)</u>	<u>N (Wt.%)</u>	<u>H/C</u>	<u>Ash</u>	<u>O&S</u>
H ₂ run liquid	87.01	5.60	1.55	.77	0.0	5.84
Steam/He run (liquid)	81.61	4.60	2.37	.67	0.0	11.42

Figure 24 Modified SESC Fractionation of
Hydropyrolysis and He/steam pyrolysis
liquids

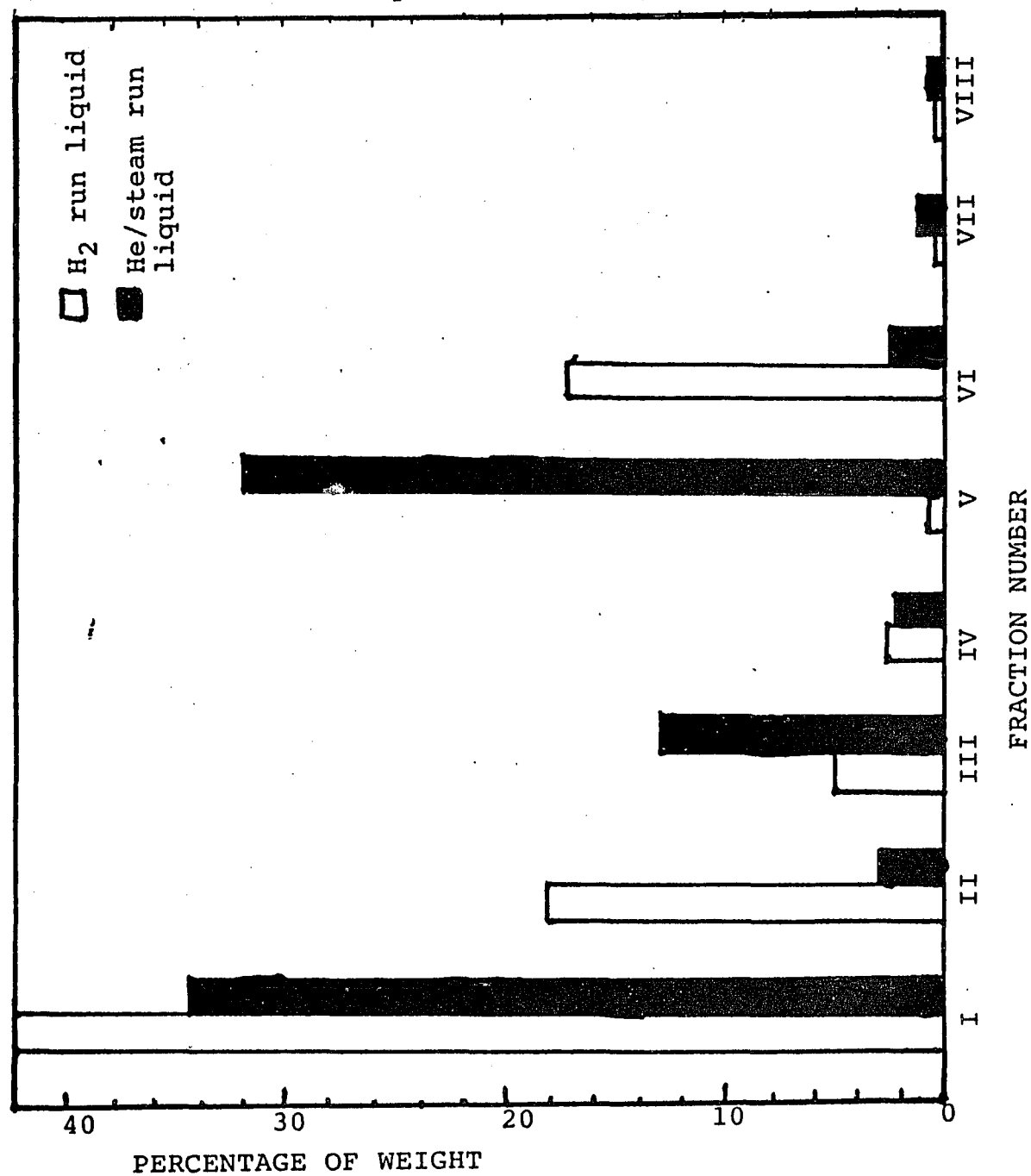


Table 14 Modified SESC Fractionation of Coal Liquids.

Fraction	<u>H₂ Run</u>	<u>Steam/He Run</u>
	Wt. %	Wt. %
I	42.1	34.27
II	17.94	2.81
III	5.30	12.78
IV	2.30	2.21
V	0.35	31.53
VI	17.84	2.39
VII	0.17	1.40
VIII	0.12	0.63
Residual*	14.00	11.98

(*Residual was calculated by material balance).

Table 15 Elemental Analyses of Modified SESC Fractions.

Fraction	<u>H₂ Run</u>				<u>Steam/He Run</u>			
	C%	H%	N%	O&S%	C%	H%	N%	O&S%
I	92.07	5.91	0.04	1.98	89.80	4.96	0.63	4.61
II	93.12	5.06	0.05	1.77	86.47	5.48	3.08	4.97
III	83.16	5.82	3.09	7.93	80.38	5.23	2.99	11.40
IV	74.11	5.76	3.11	17.02	78.27	4.90	2.81	14.02
V	73.08	6.24	3.18	17.50	72.19	7.88	1.21	18.72
VI	72.20	7.01	5.44	15.36	75.21	5.16	2.89	16.74
VII	64.01	3.84	3.31	28.84	71.90	6.78	0.83	20.49
VIII	(insufficient amount of sample)				71.35	8.26	0.76	19.63

(* By material balance).

The G.C. boiling point distribution curves for both volatile liquids and their fractions are given in figures 25 to 33. Figures 25 and 31 show the boiling point distribution curves for the coal liquids before fractionation. Figures 26 and 27 show the boiling point curve for fraction I of hydrogen run. Figure 27 shows the curve obtained after prolonged heating at 100 C of the sample under vacuum. Some components (eg. naphthalene, appearing in the 250 C region) are lost during the treatment.

Boiling point analysis of each of the modified SESC fractions for both liquids did show a range of 50 to 400 C for fraction I, and 300 - 550 C for fraction II and fraction III. Fraction IV and higher did not elute from the gas chromatograph column, and hence, their boiling points could be higher than 550 C (Figure 30). Although the boiling point distribution curves were similar for corresponding fractions of both liquids, it should be noted that the relative proportions of each fraction are different in both liquids, as a consequence the overall boiling point distributions of the two liquids are different.

The steric exclusion HPLC molecular size distribution curve of the hydrogen run liquids shows a bimodal distribution. No such behavior was seen in the steam/helium run which showed a unimodal distribution of higher molecular weight.

Figure 25 Simulated B.P. Curve
of hydrogen run liquids

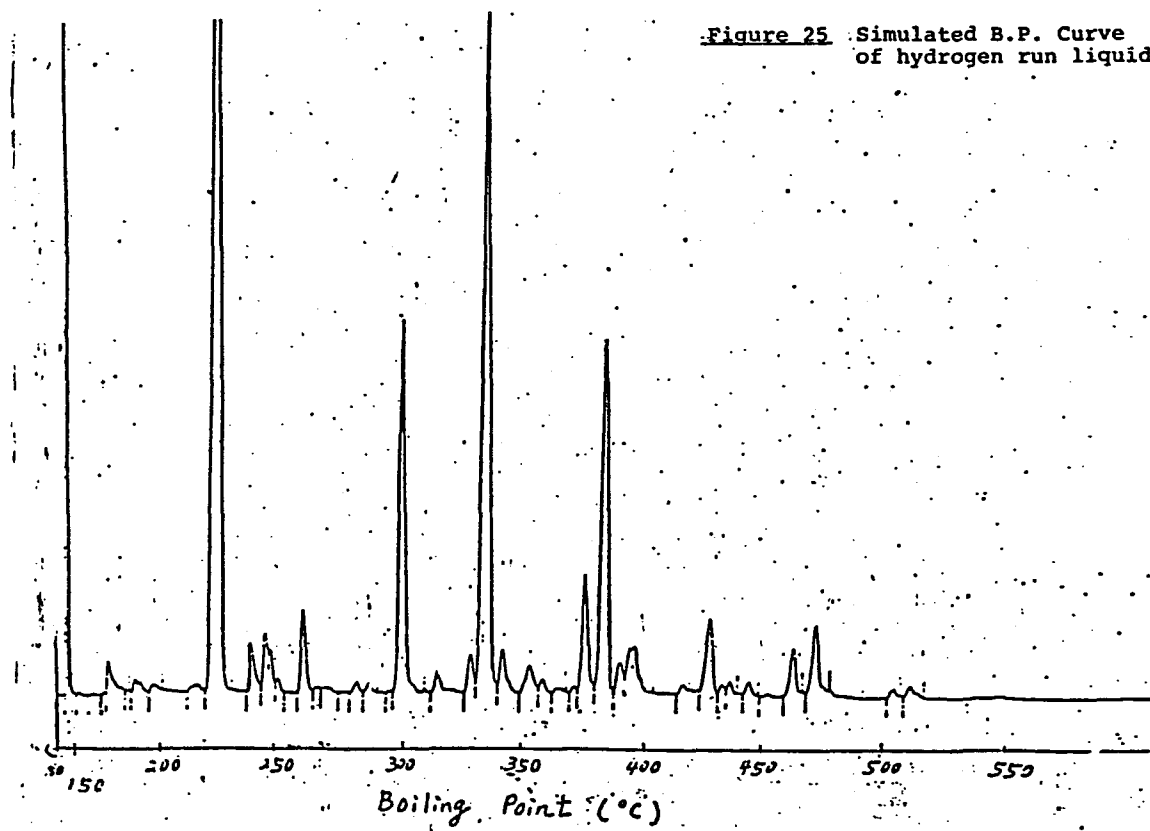


Figure 26 Simulated B.P. Curve
hydrogen run Fraction I
before solvent evaporation

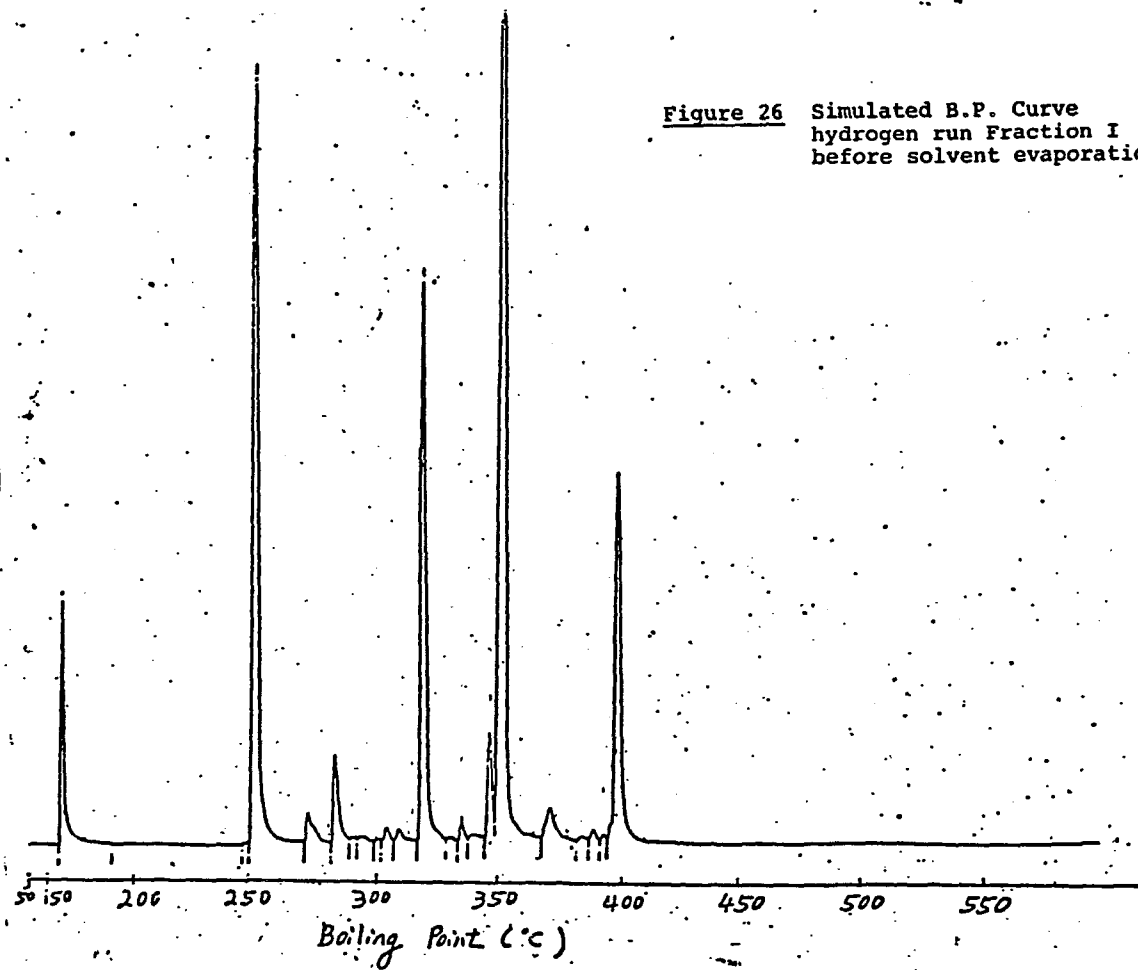
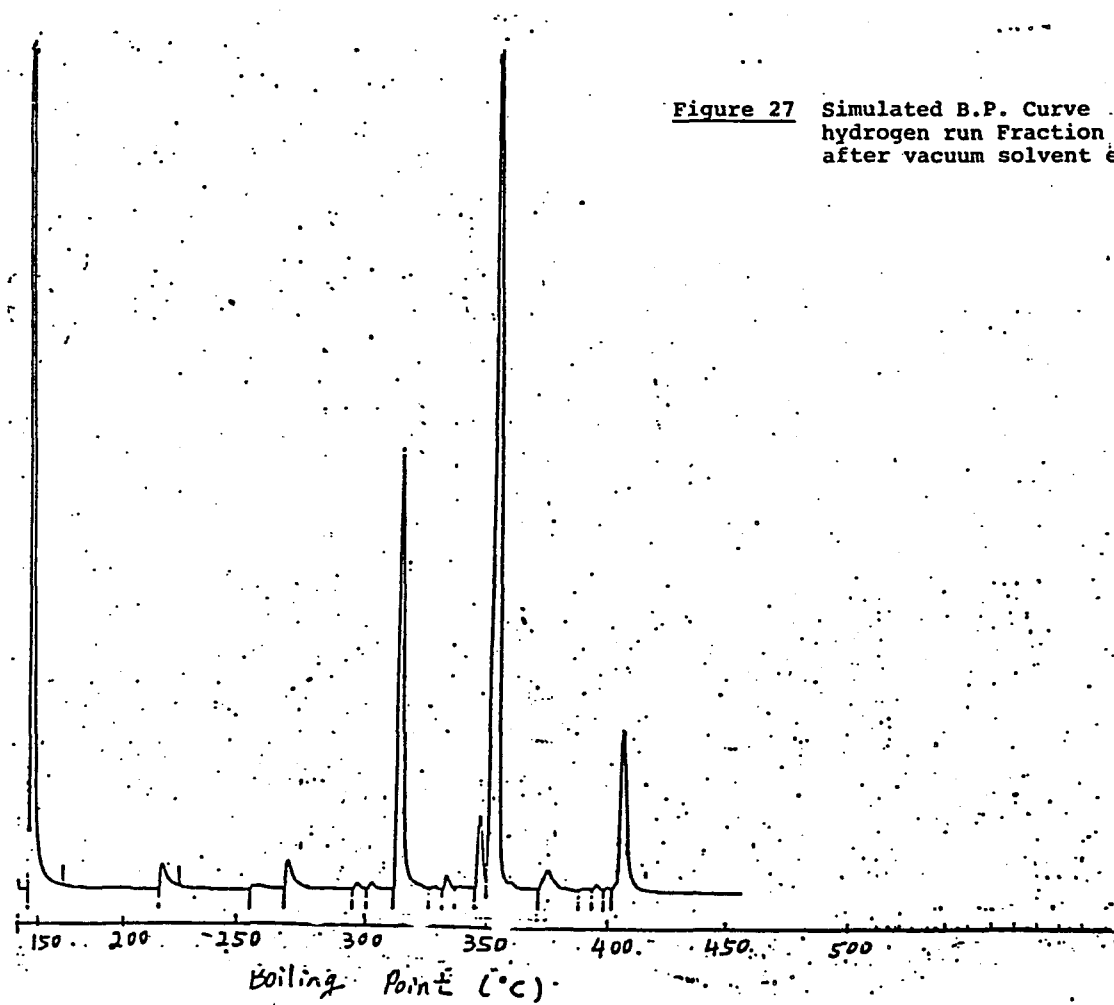


Figure 27 Simulated B.P. Curve
hydrogen run Fraction I
after vacuum solvent evaporation



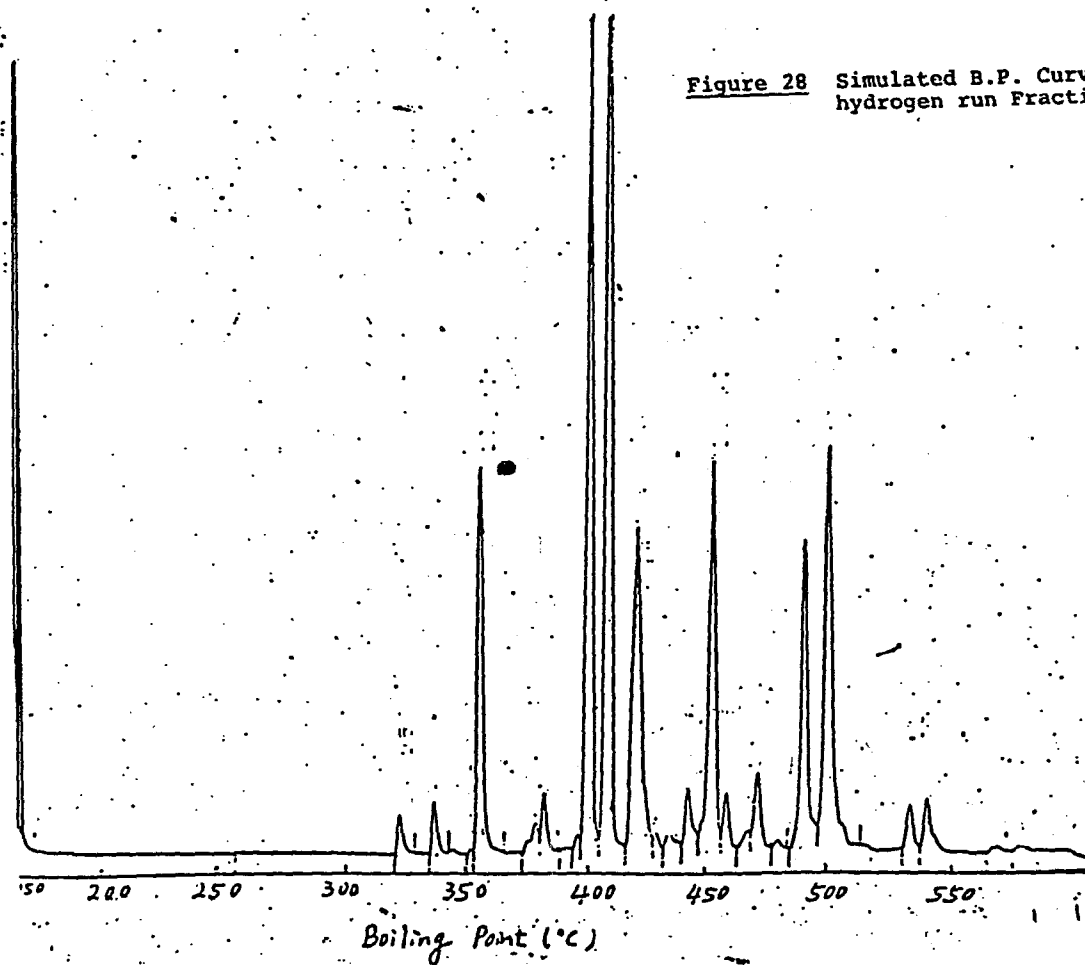


Figure 28 Simulated B.P. Curve
hydrogen run Fraction II

Figure 29 Simulated B.P. Curve of hydrogen run Fraction III

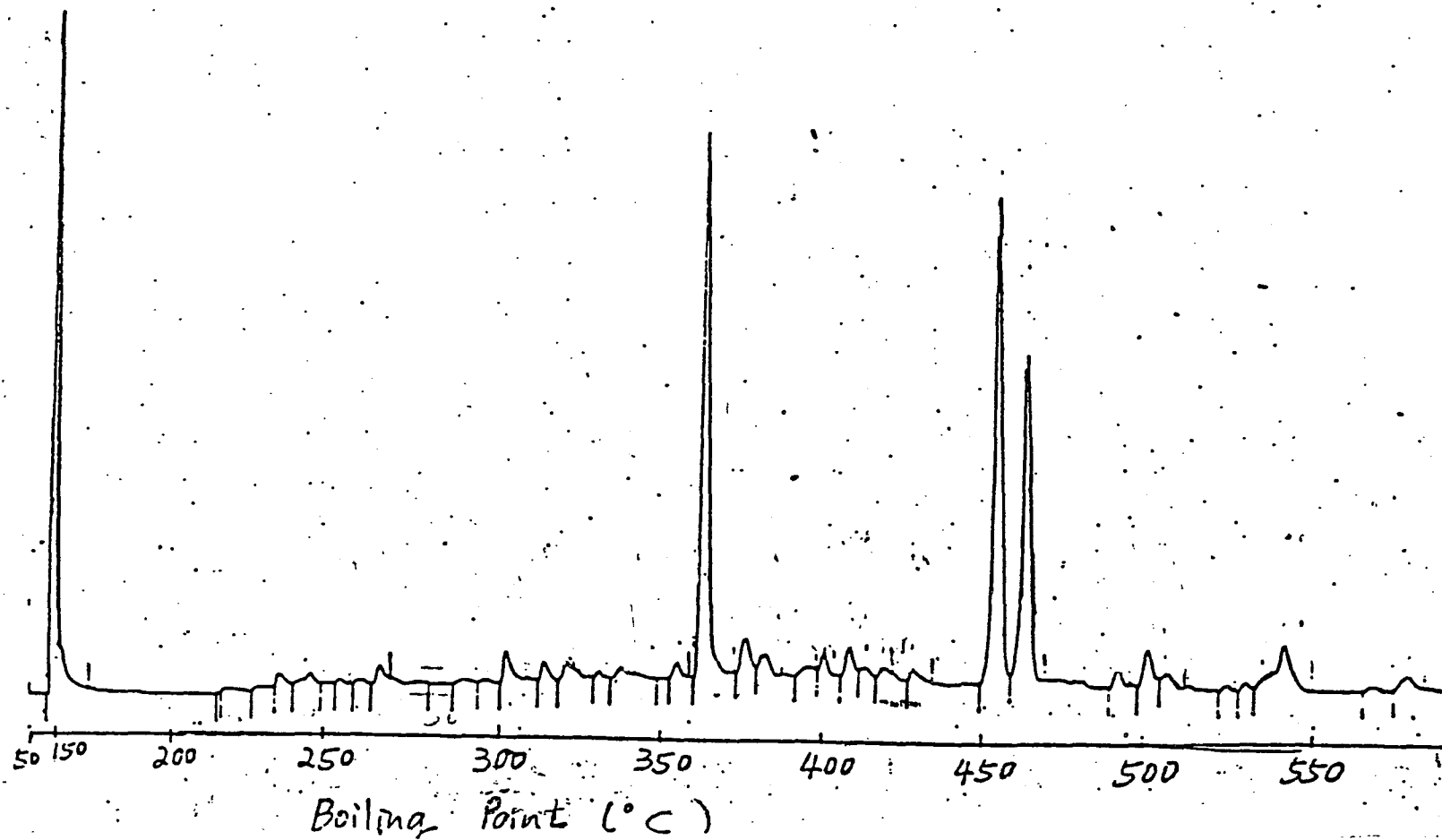


Figure 30 Simulated B.P. Curve of hydrogen run liquid Fraction IV

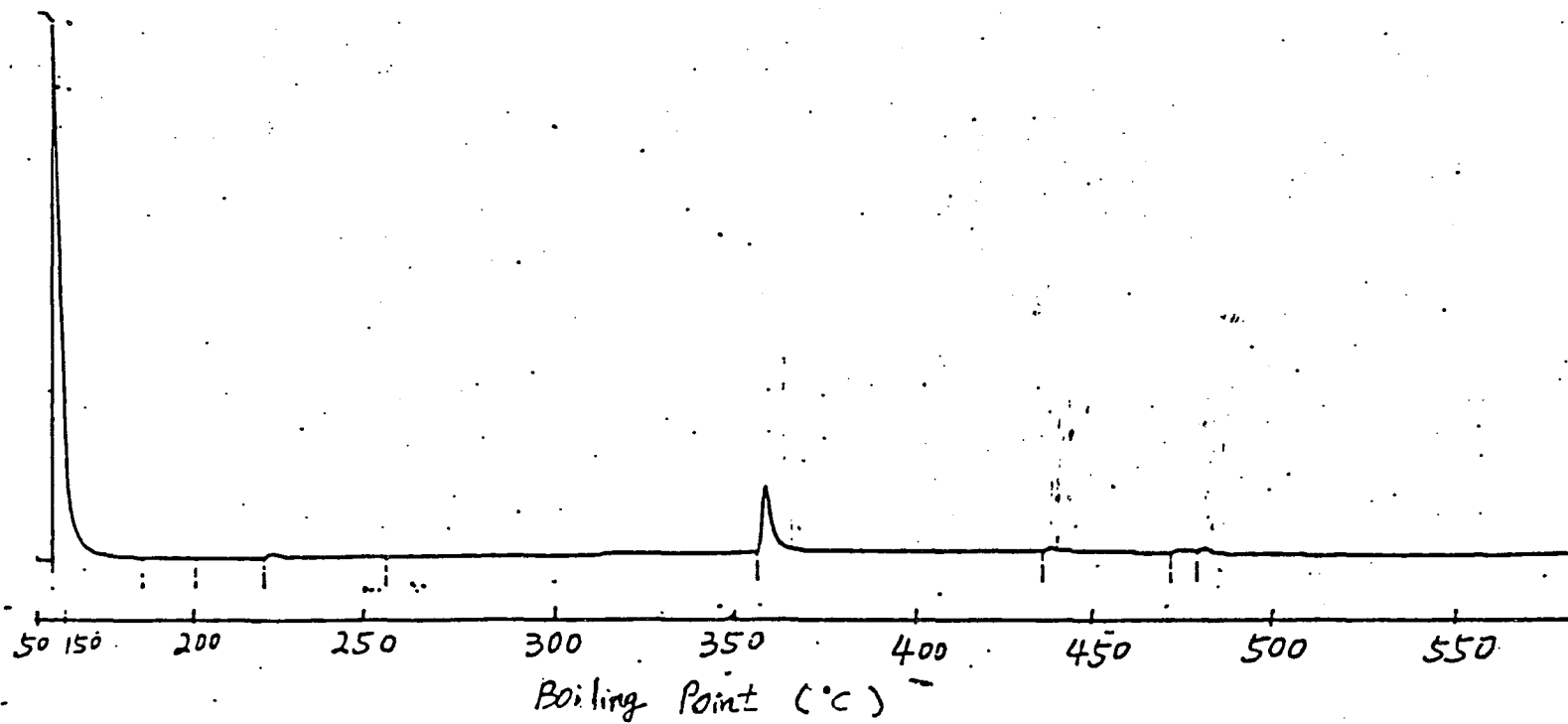
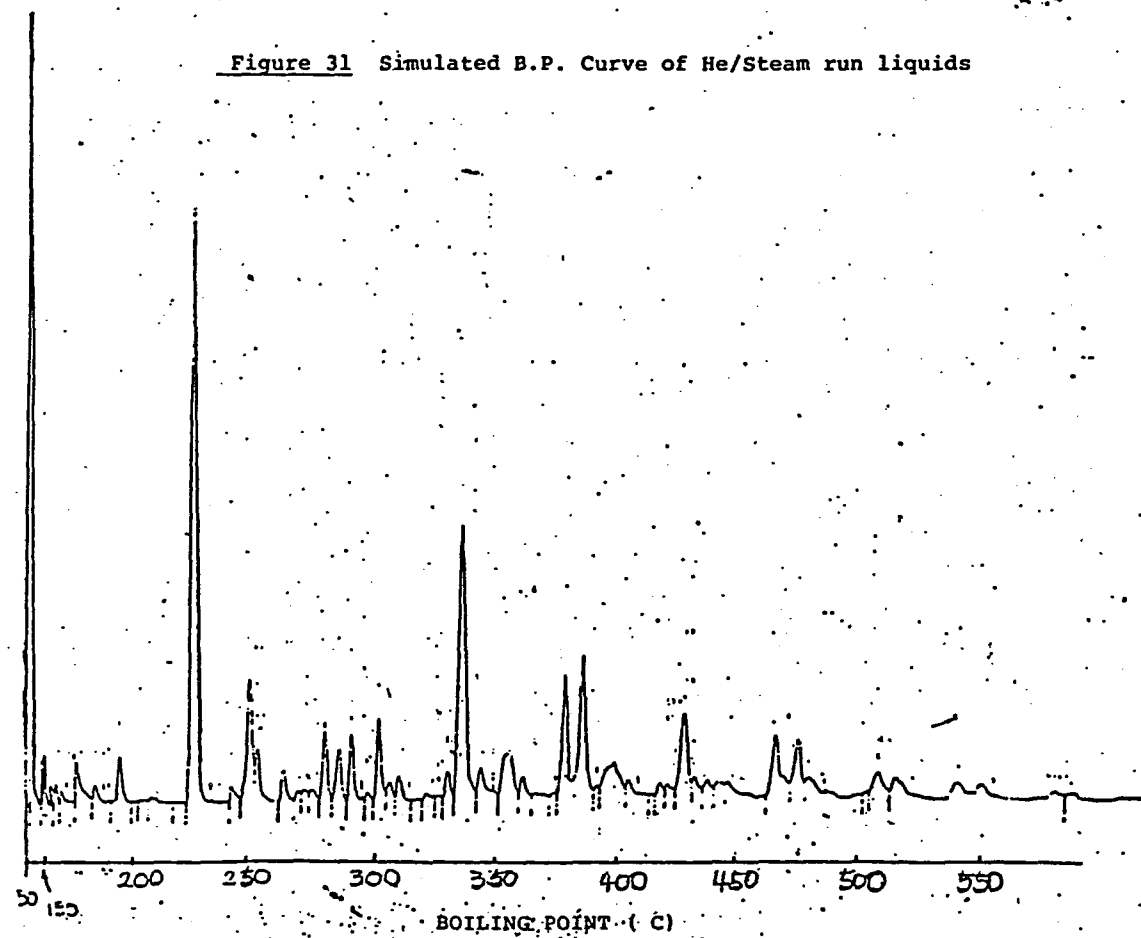


Figure 31 Simulated B.P. Curve of He/Steam run liquids



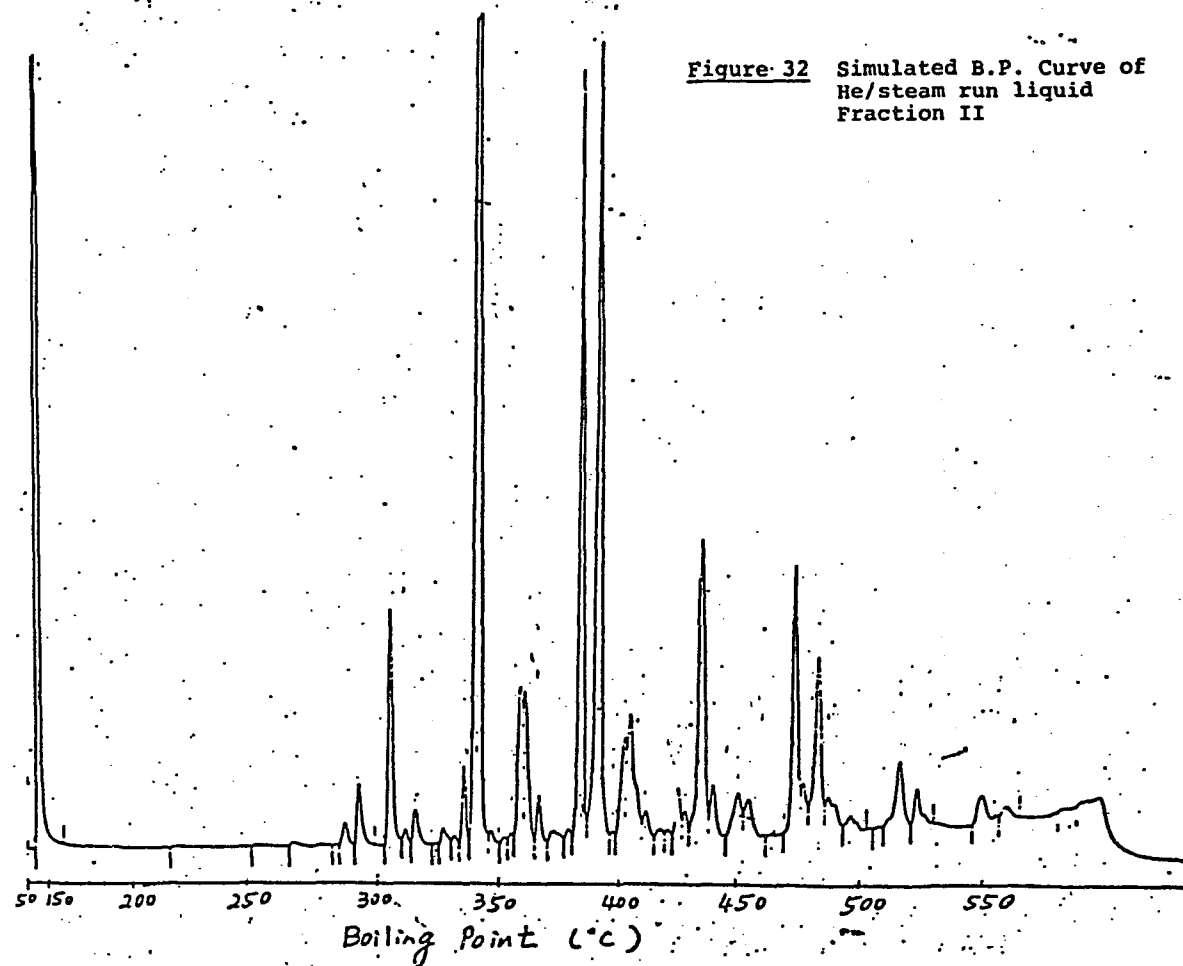
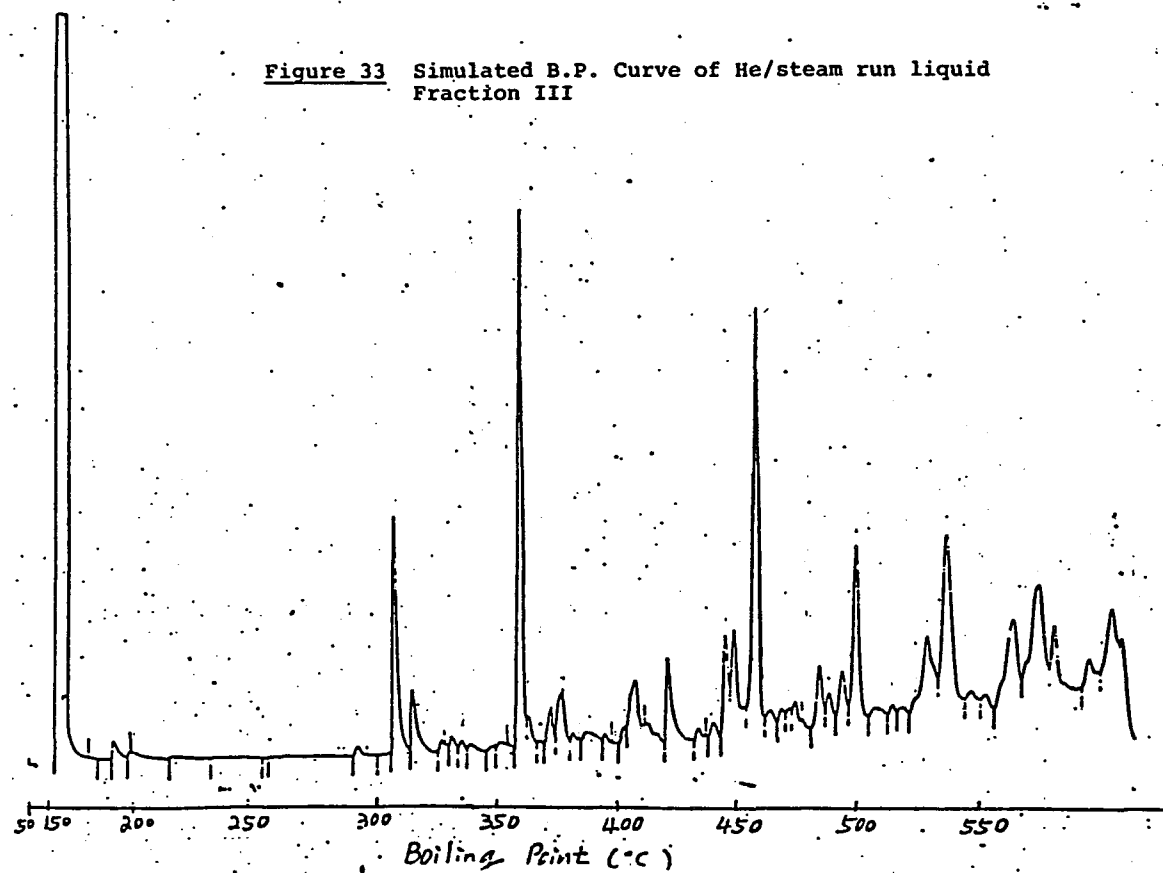


Figure 33 Simulated B.P. Curve of He/steam run liquid
Fraction III



There is only a single peak for each of hydrogen run fraction I to fraction III. The elution time of samples decreases and also the molecular weight is increased with the fraction number increased. The curves of both hydrogen run fractions IV and V are peaks with shoulders. The peaks of hydrogen run fractions VI and VII both present a bimodal distribution in which the smaller peaks eluted first. Whereas, the distribution for hydrogen run fraction VIII is tri-modal, and covers the range of molecular weight from 80 to 5000.

The molecular weight distribution curve of fraction I of steam-helium run is bimodal in the range of less than 200 . One of these is less than 80 which is outside the range of calibration. Fraction II has a sharp peak and the peak of fraction III is more rounded. While the molecular weight distribution curves of fractions IV and V are both bimodal, fraction VI presents a single peak and the molecular weight distribution of fractions VII and VIII both present four different peaks.

From the molecular weight distribution curves, the number-average molecular weight and the weight-average molecular weight were calculated with formulas given by Schanne and Haemel (1981). The average molecular weights of the total liquids and modified SESC fractions are given in Table 16. The results are presented graphically in figure 34.

Table 16

Average Molecular Weights
(Calculated by Steric Exclusion HPLC Method)

<u>H₂ Run</u>			<u>Steam/He Run</u>		
<u>Fraction</u>	<u>Mn</u>	<u>Mw</u>	<u>Fraction</u>	<u>Mn</u>	<u>Mw</u>
Total Liquid	125	165	Total Liquid	209	276
I	164	193	I	93	121
II	179	216	II	150	197
III	392	480	III	262	331
IV	368	546	IV	267	402
V	414	691	V	301	806
VI	234	425	VI	202	246
VII	301	574	VII	416	819
VIII	329	749	VIII	431	953

$$M_n = \frac{\sum_{i=1}^n H_i}{\sum_{i=1}^n \frac{H_i}{M_i}} = \text{Number average molecular weight}$$

$$M_w = \frac{\sum_{i=1}^n H_i M_i}{\sum_{i=1}^n H_i} = \text{Weight average molecular weight}$$

where H_i is the peak height of molecular species
 M_i is the molecular weight of molecular species

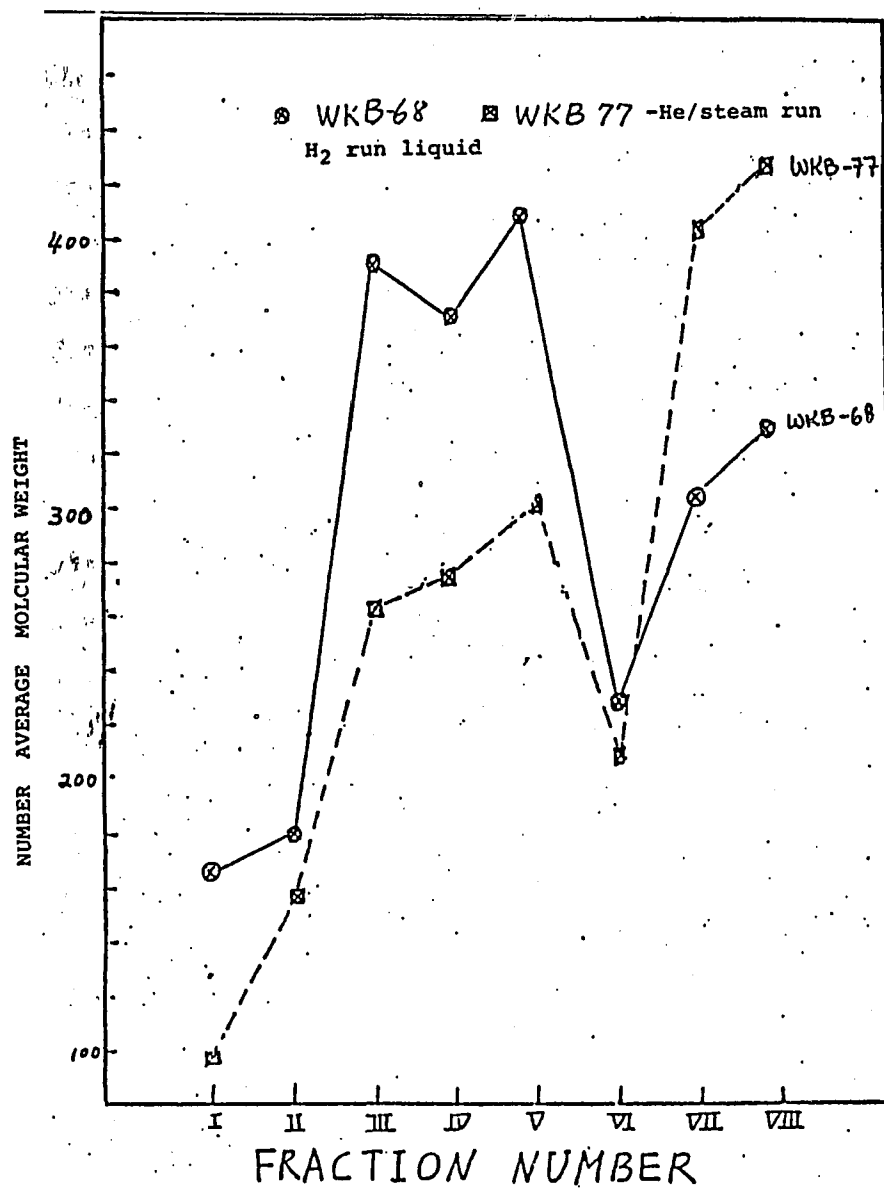


Figure 34 Molar-Average Molecular Weight vs. Fraction Number

The hydrogen-NMR spectra obtained for the coal liquid samples and their modified SESC fractions are presented in figures 35 to 54. Table 17 summarizes the information obtained from H-NMR spectroscopy with respect to the aromaticity of the samples and fractions analyzed.

The whole liquid sample obtained in steam-helium run showed a higher aromatic hydrogen content than hydrogen run. As shown in table 17, the distribution of aromatic hydrogen in modified SESC fractions of steam-helium run and hydrogen run are comparable for only the first two fractions (non-polar aromatics). Fraction III of steam-helium run (the polar aromatic with non-basic N, O, and S heterocyclics) has a larger percentage of the whole material and is more aromatic than the corresponding fraction of hydrogen run. A comparison of the fractions IV shows large differences in the aromatic hydrogen content of the two liquids. Hydrogen run fraction IV is more aliphatic in nature than 77 fraction IV. The characteristic monophenols of fraction IV showed up in the 4 to 5 ppm region of the steam-helium run spectrum appeared shifted and much reduced in the hydrogen run spectrum. The aromatic hydrogen content of the hydrogen run fraction IV is much less than that of the same fraction of the 77 sample. And also notice that hydrogen run fraction IV has higher molecular weight than steam-helium run.

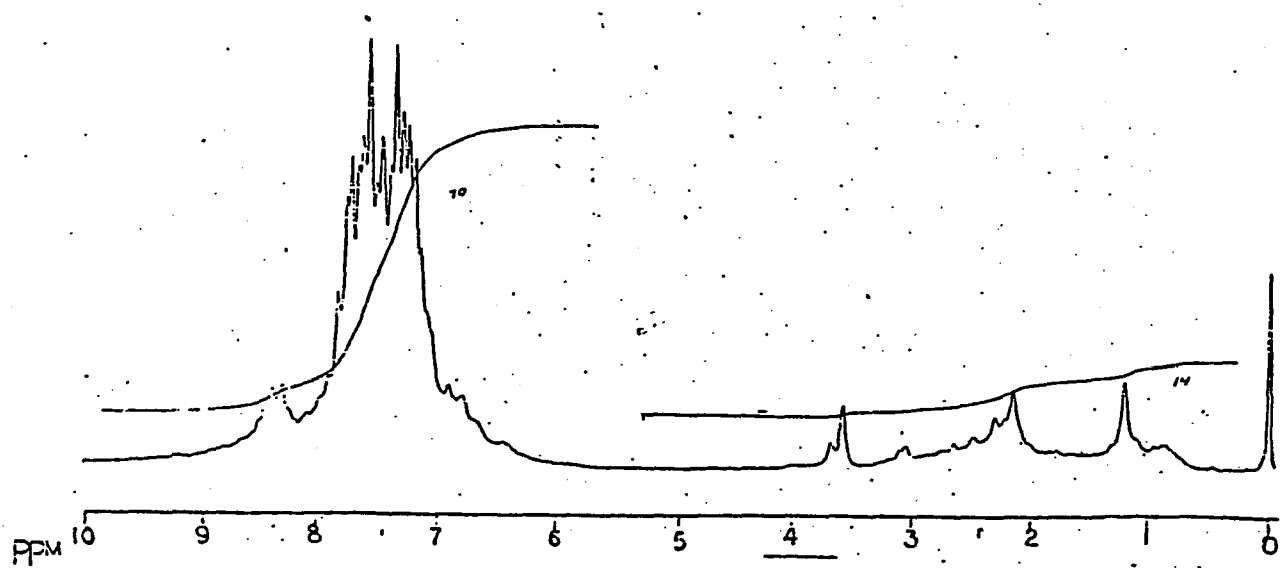


Figure 35. WKB 68 Whole Liquid

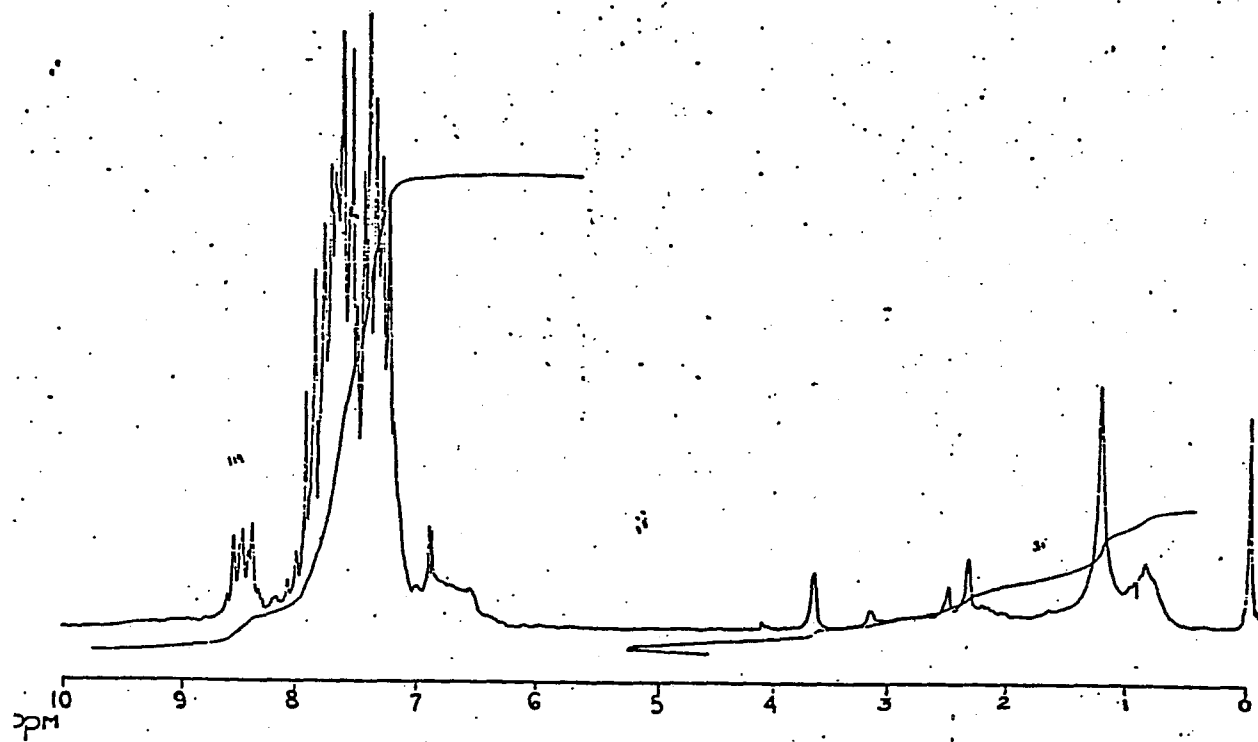


Figure 36 WKB-68 Fraction I

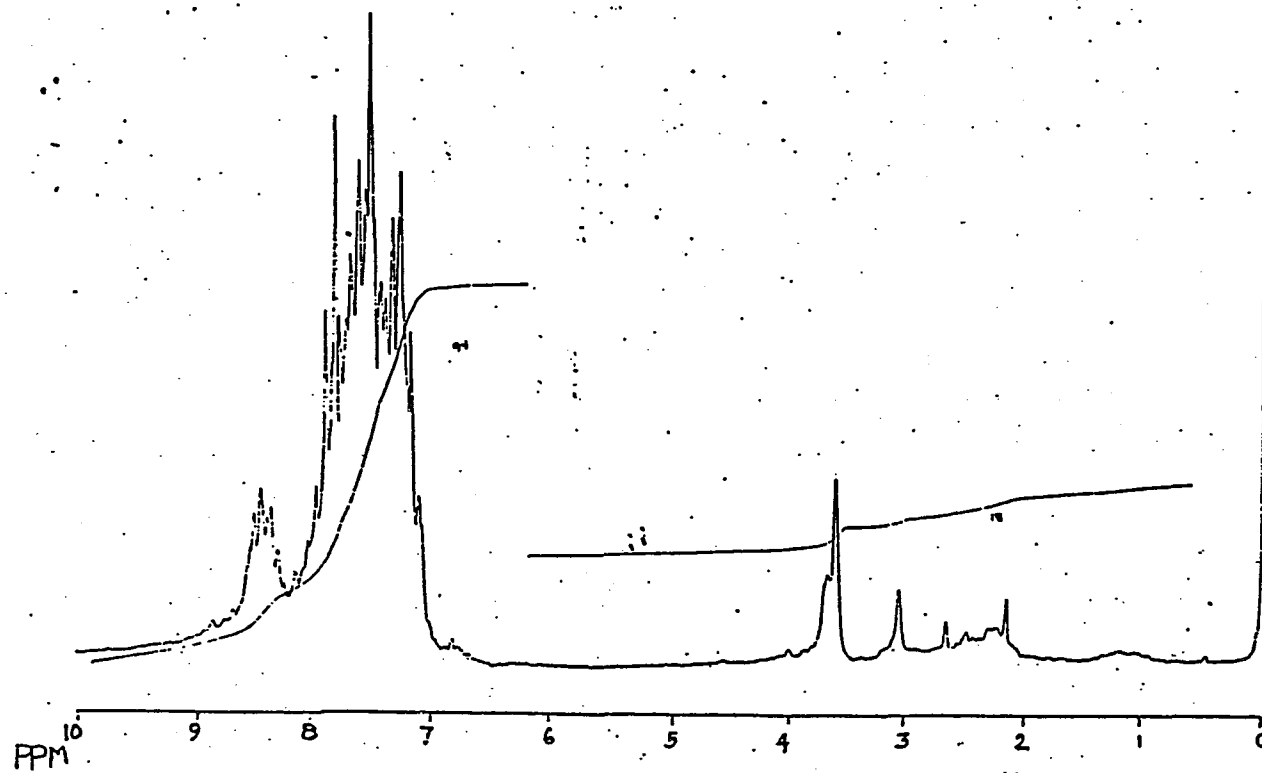


Figure 37 WKB-68 Fraction II

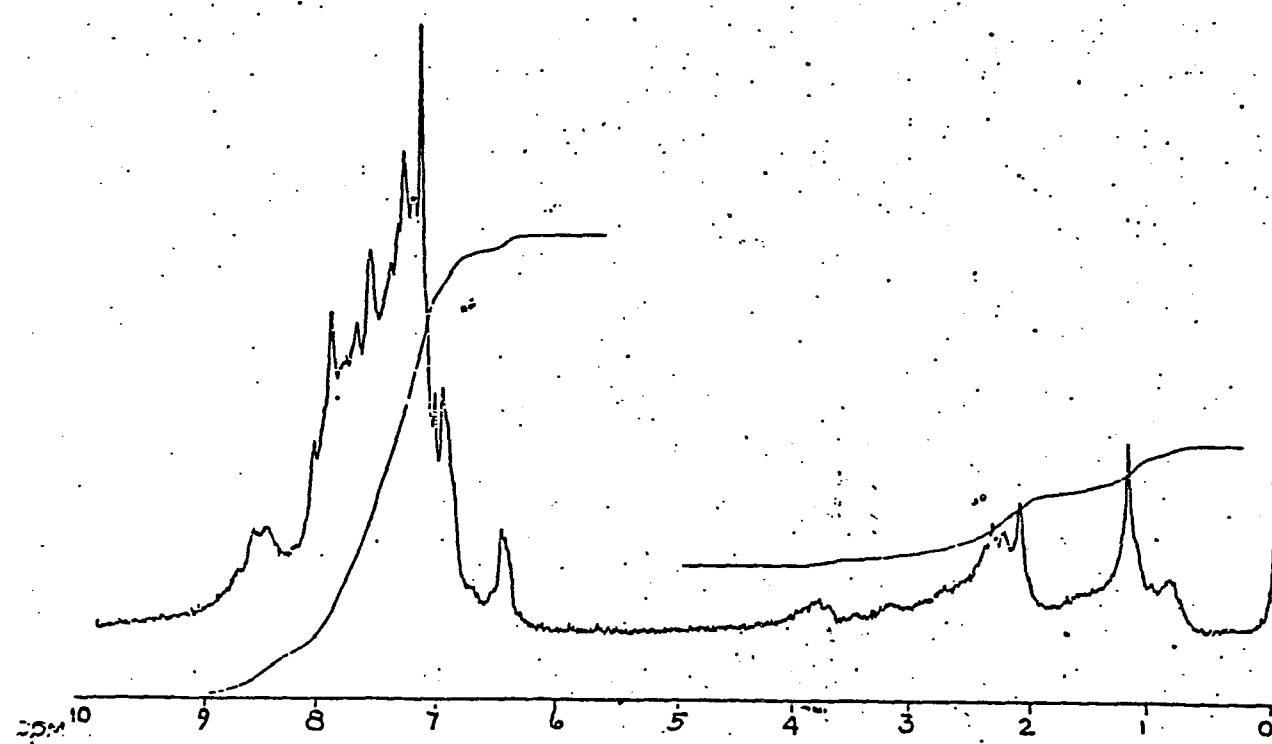


Figure 38 WKB-68 Fraction III

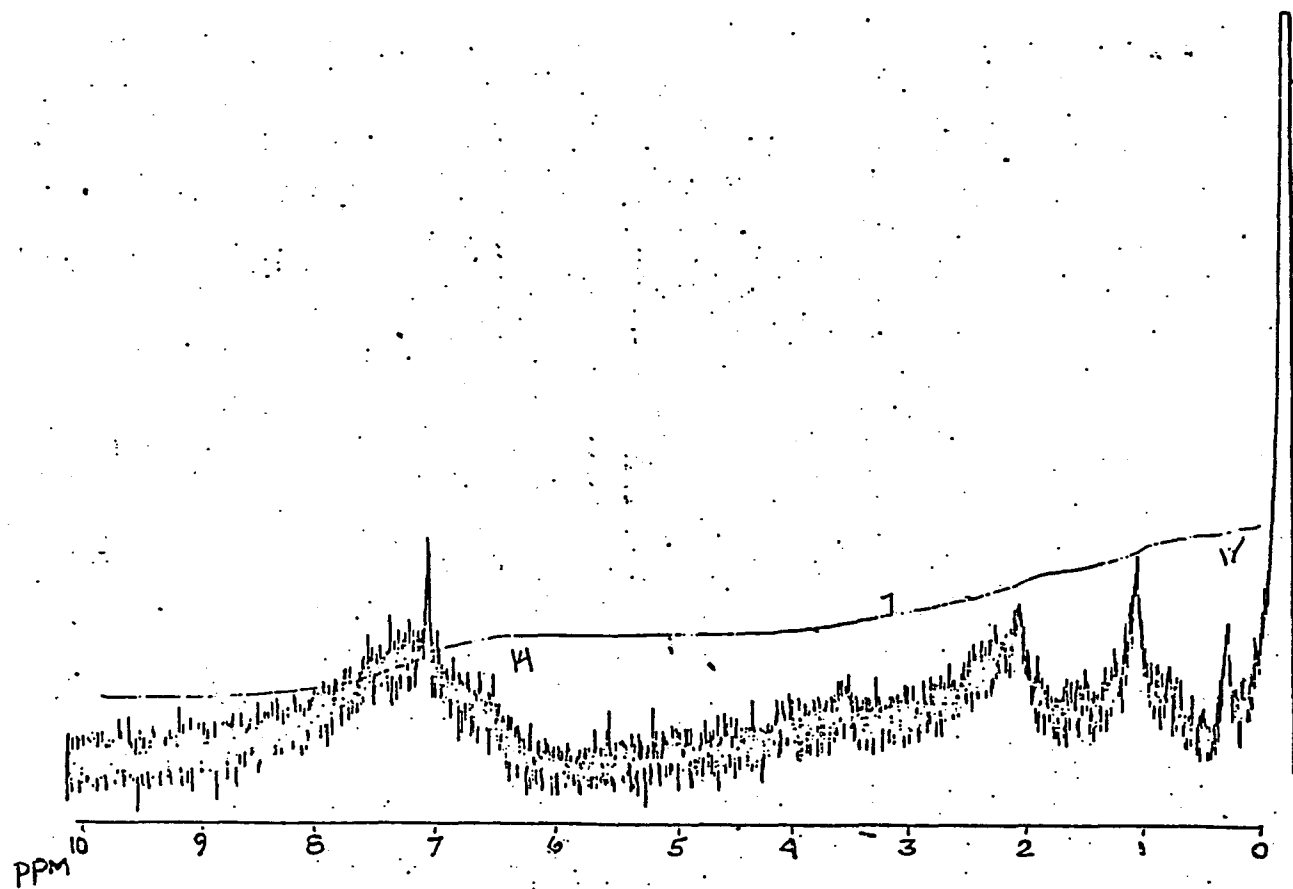


Figure 39 WKB-68 Fraction IV

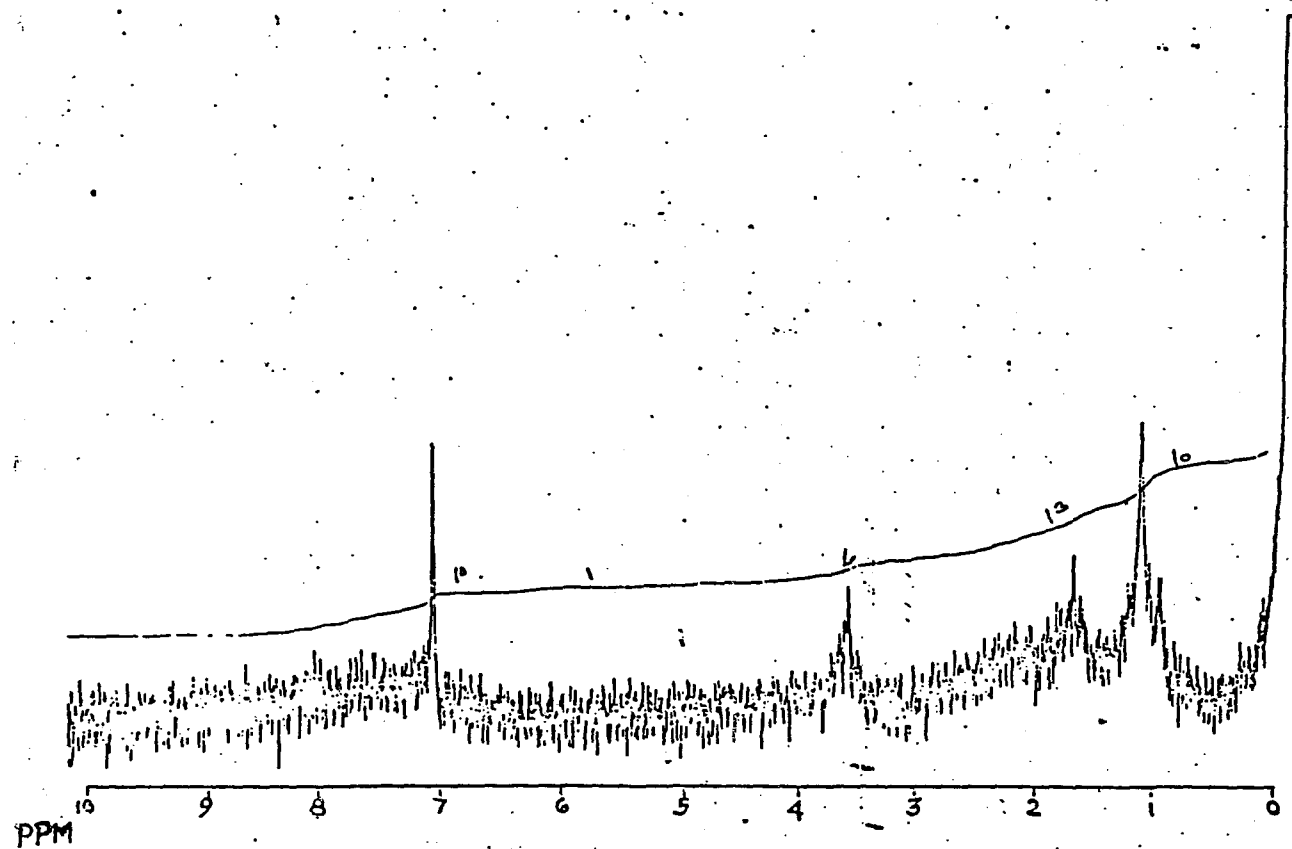


Figure 40 WKB-68 Fraction V

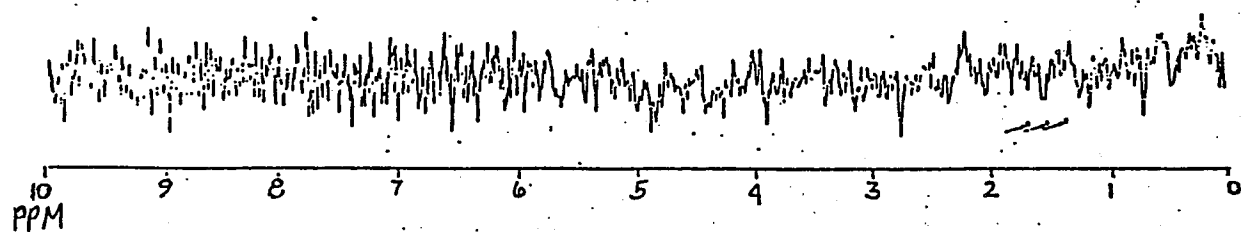


Figure 41 WKB-68 Fraction VI

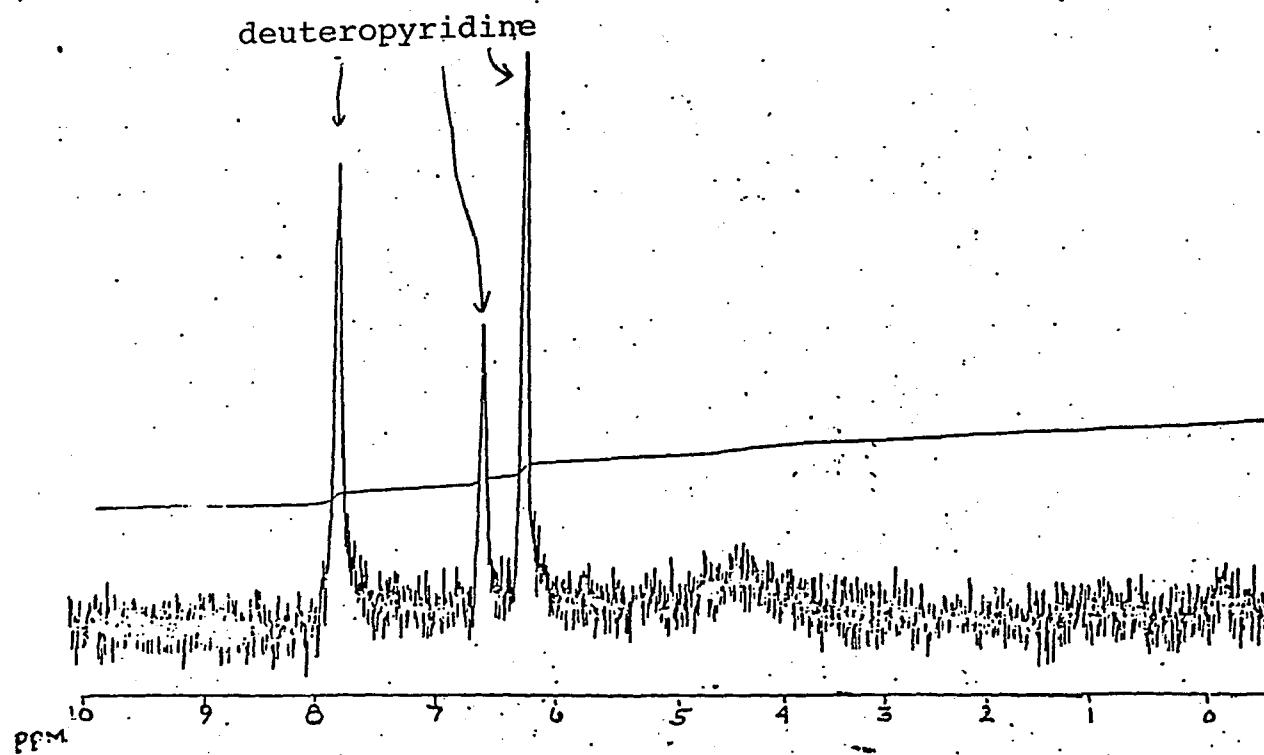


Figure 42 WKB-68 Fraction VII

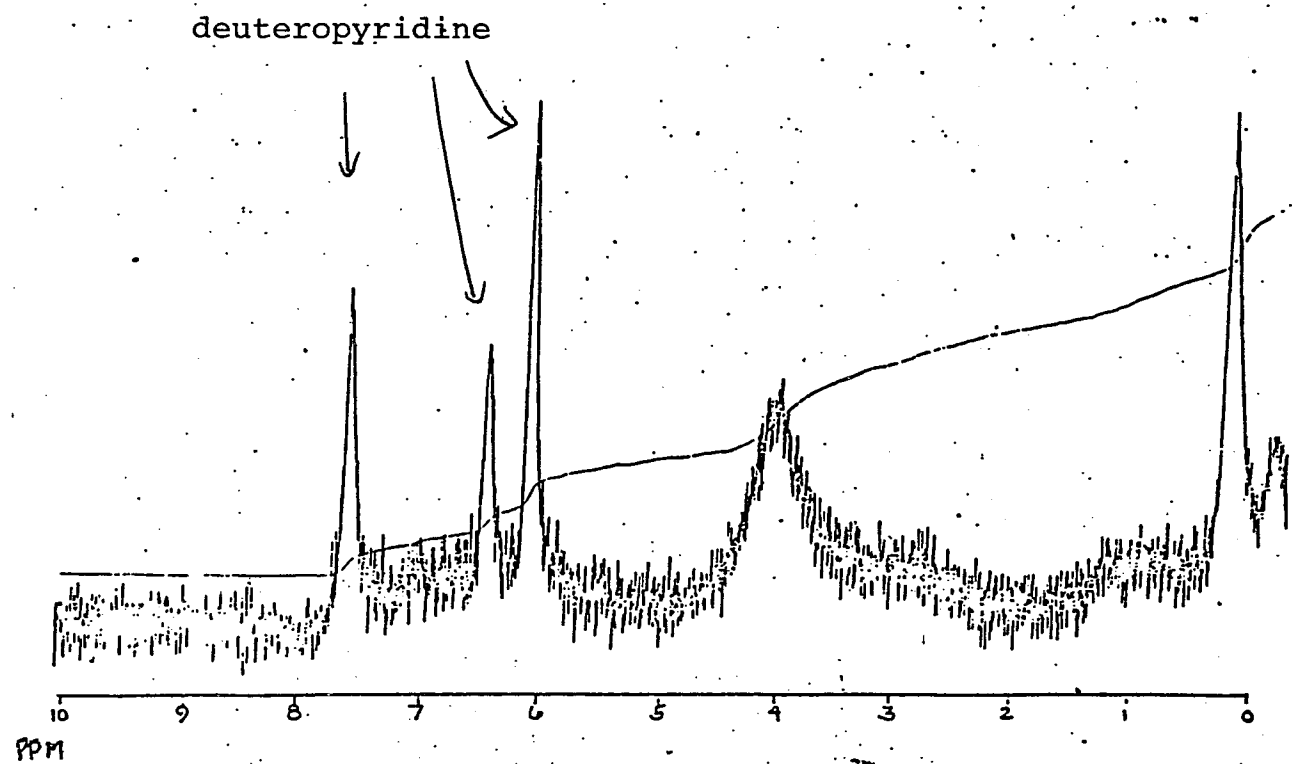


Figure 43 WKB-68 Fraction VIII

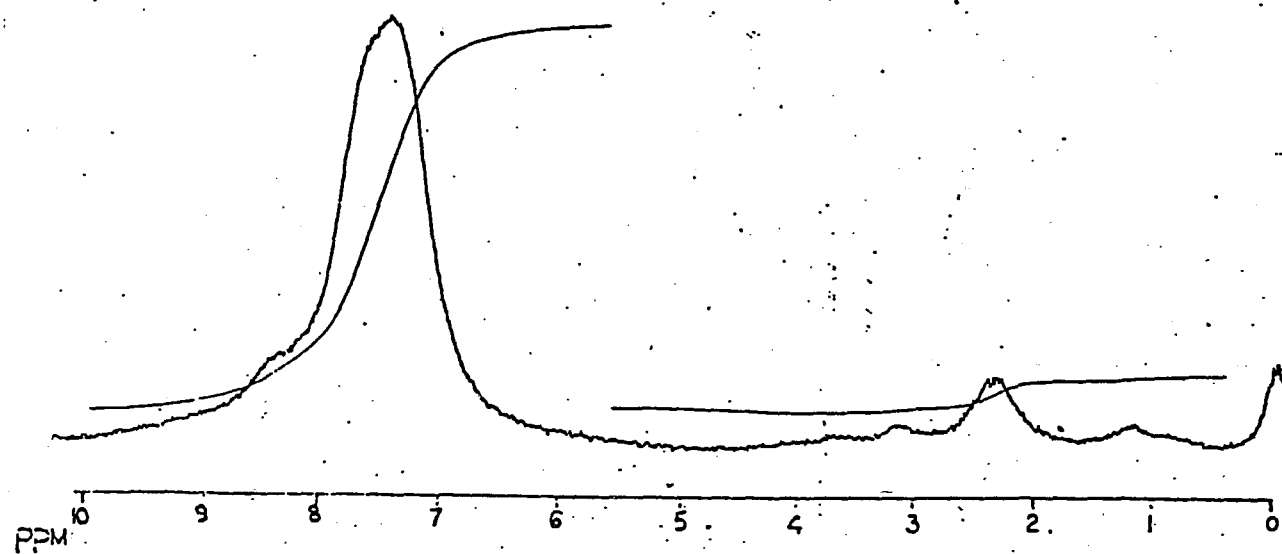


Figure 44 WKB-77 Acetone Wash Liquid

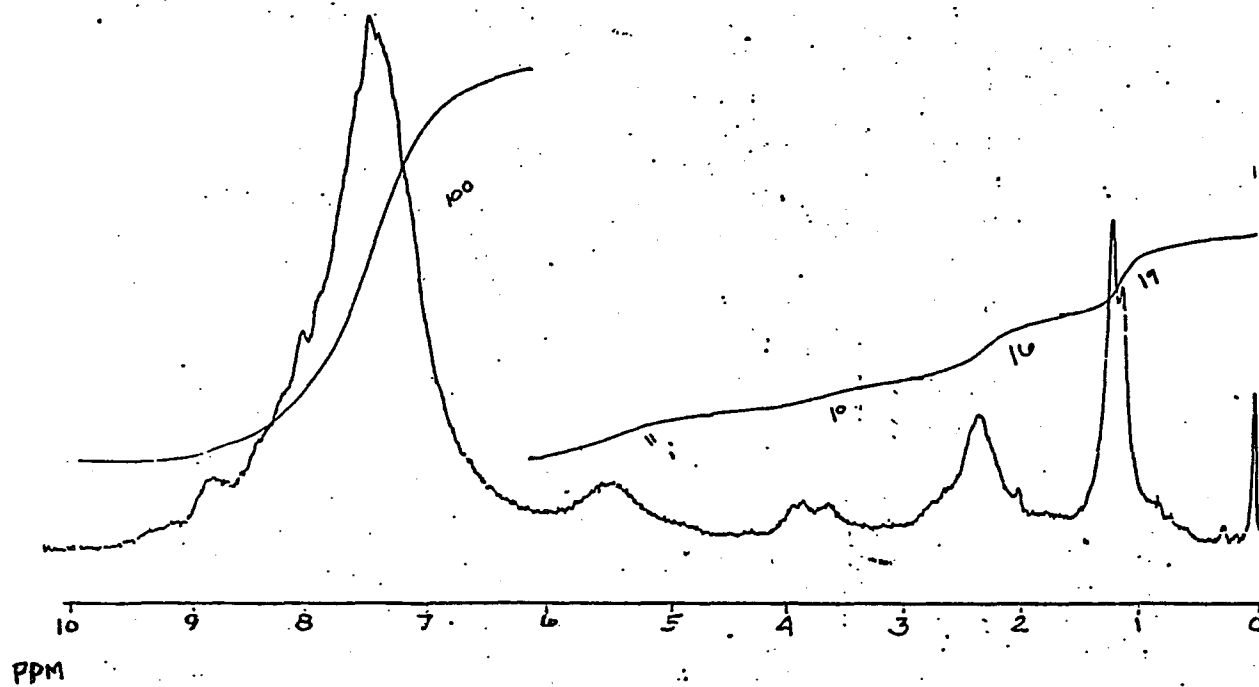


Figure 45 WKB-77 Liquid

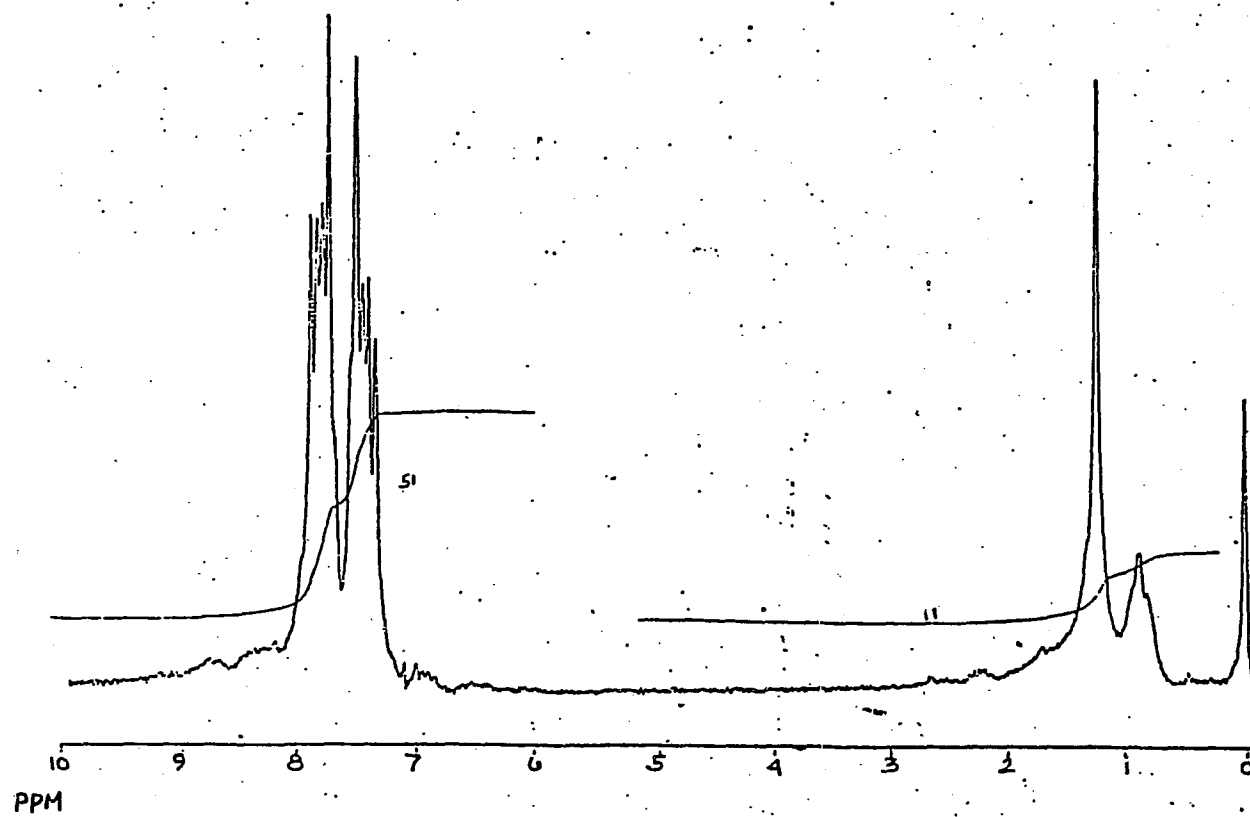


Figure 46 WKB-77 Fraction I

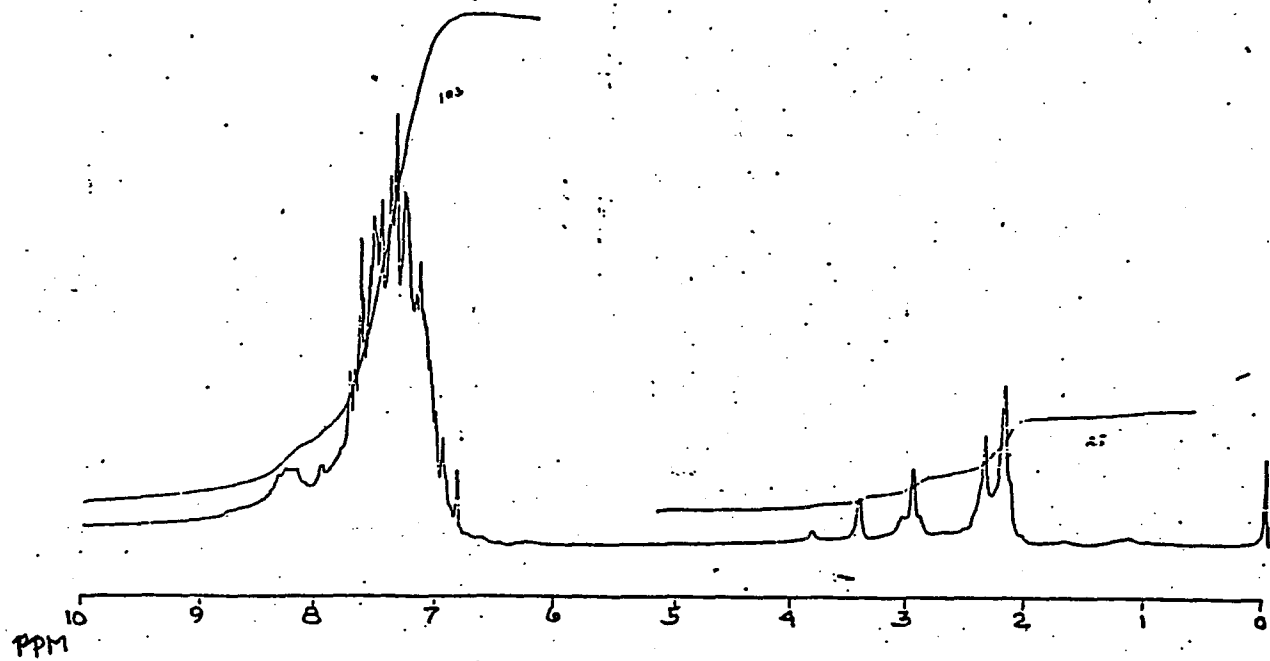


Figure 47 WKB-77 Fraction II

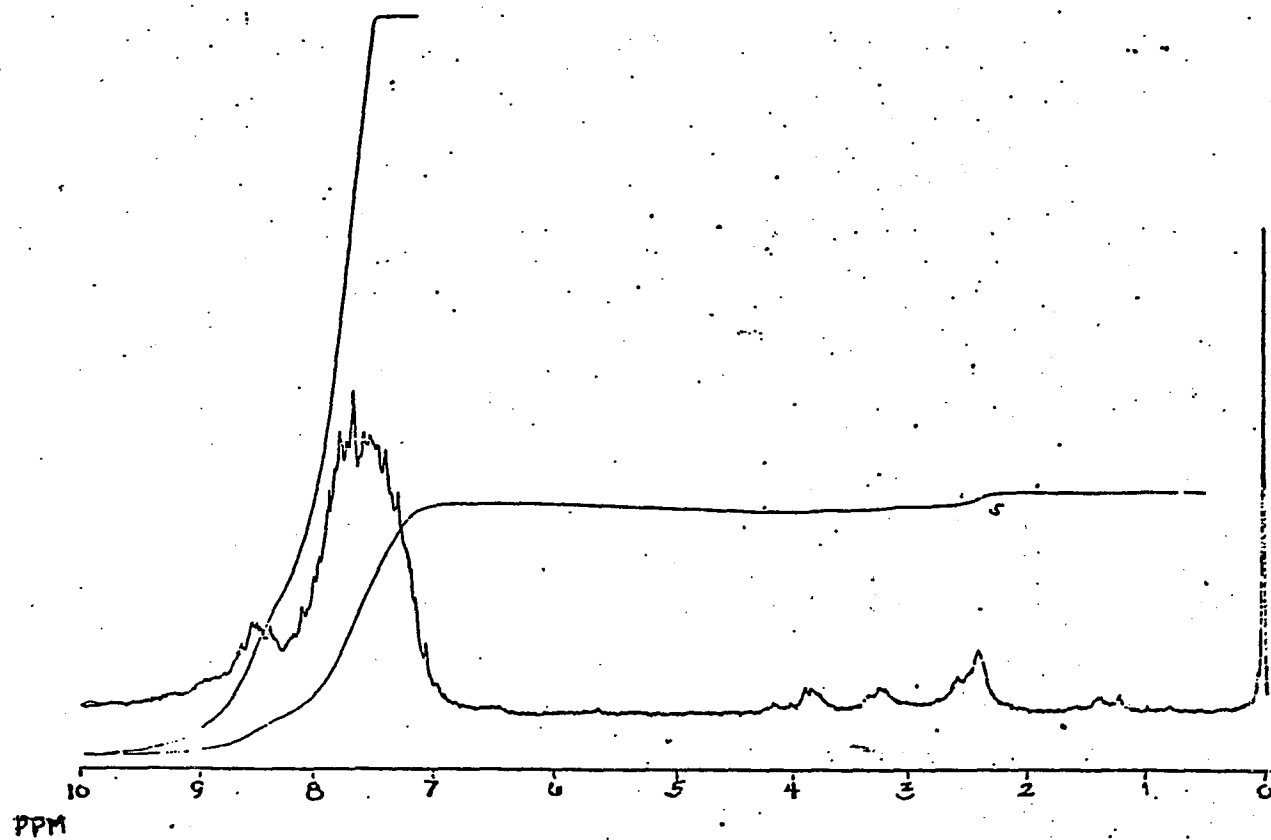


Figure 4B WKB-77 Fraction III

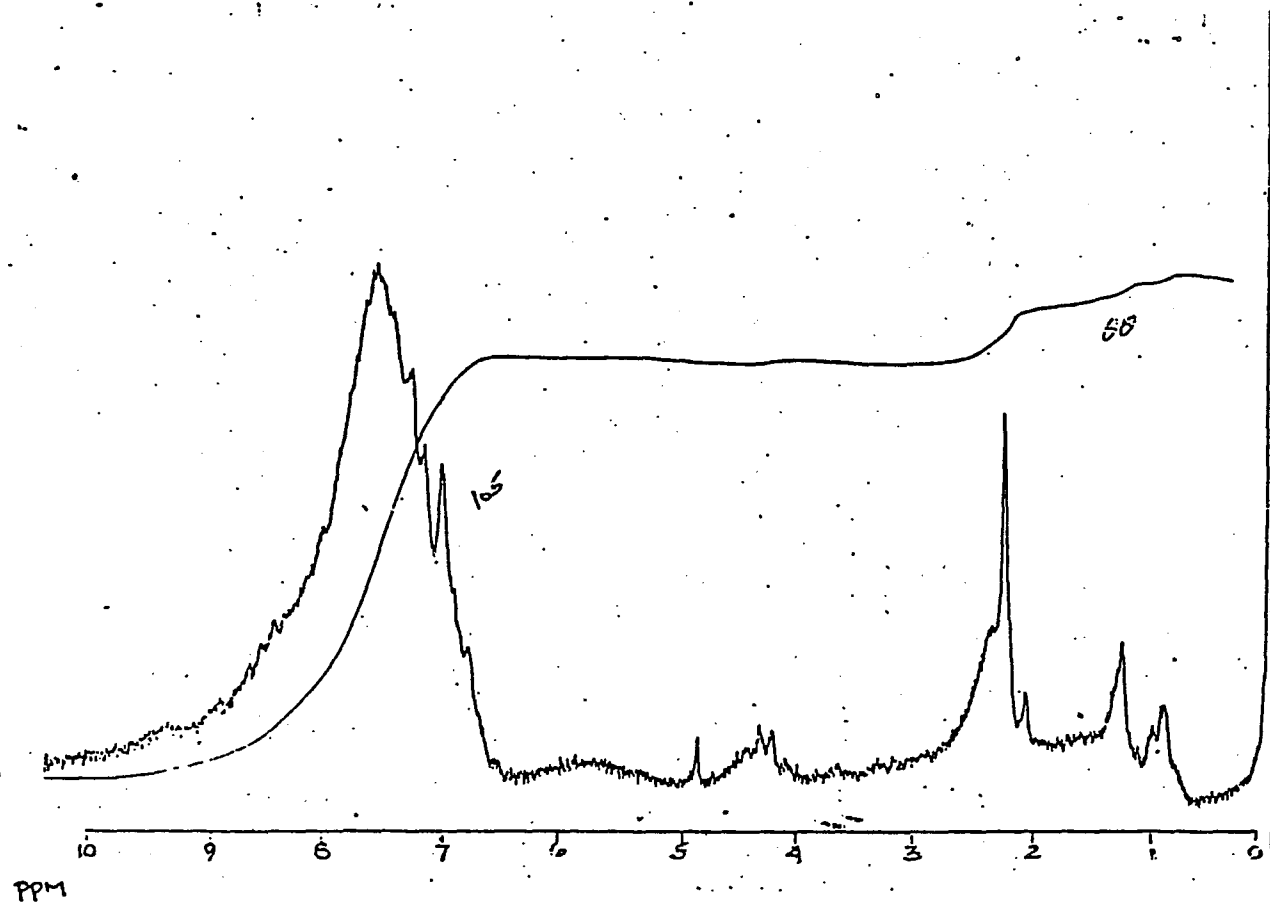


Figure 49 WKB-77 Fraction IV

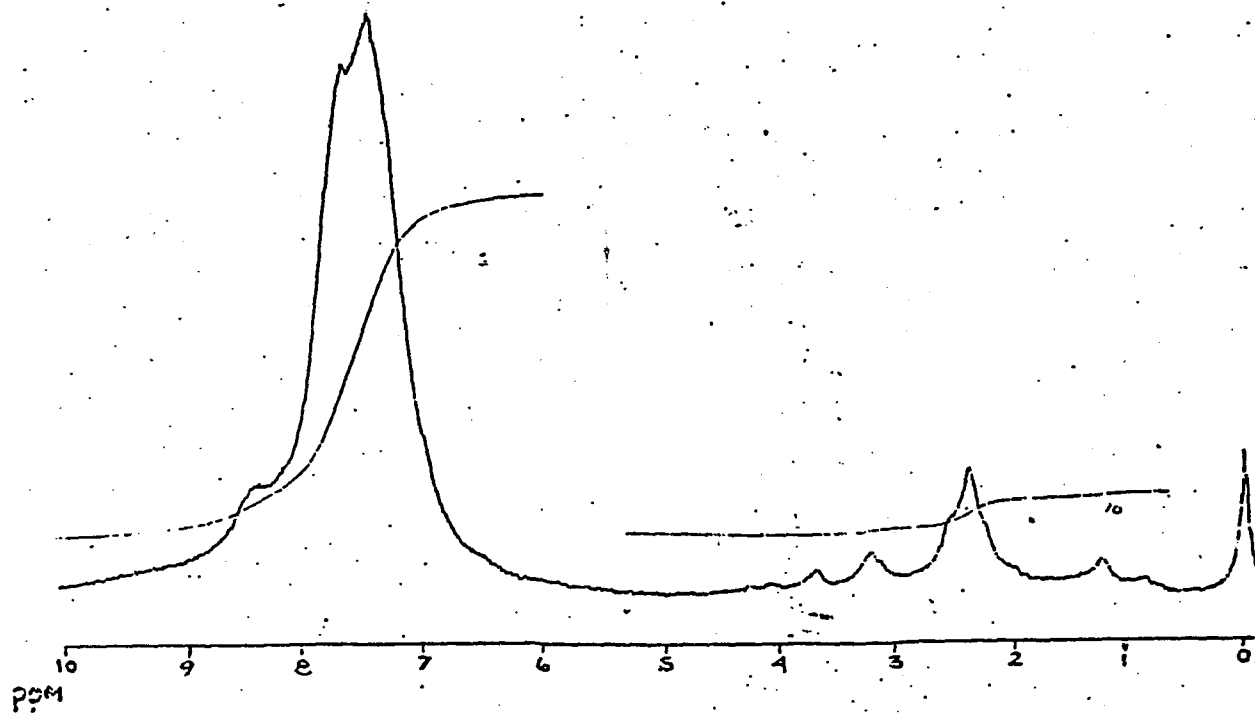


Figure 50 WKB-77 Fraction V

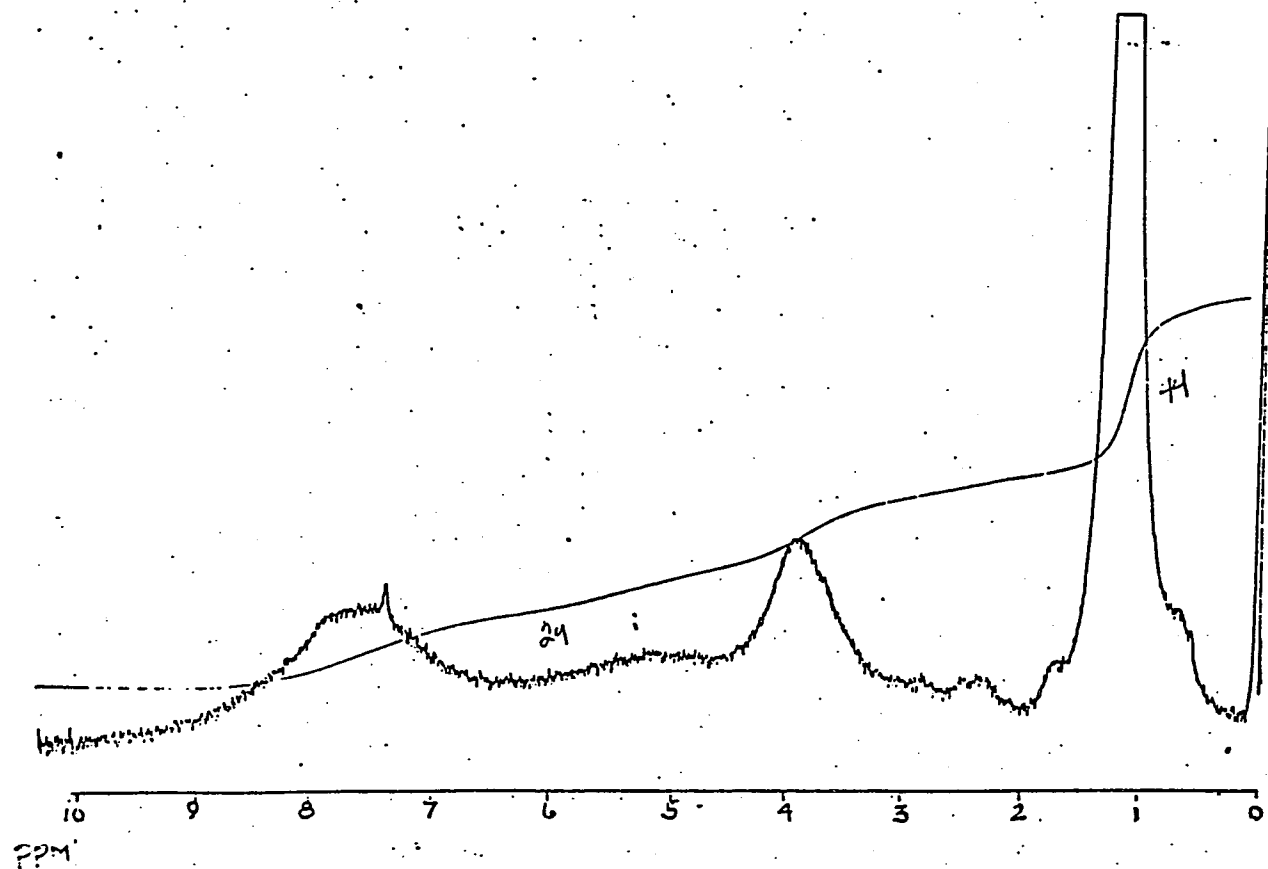


Figure 51 WKB-77 Fraction VI

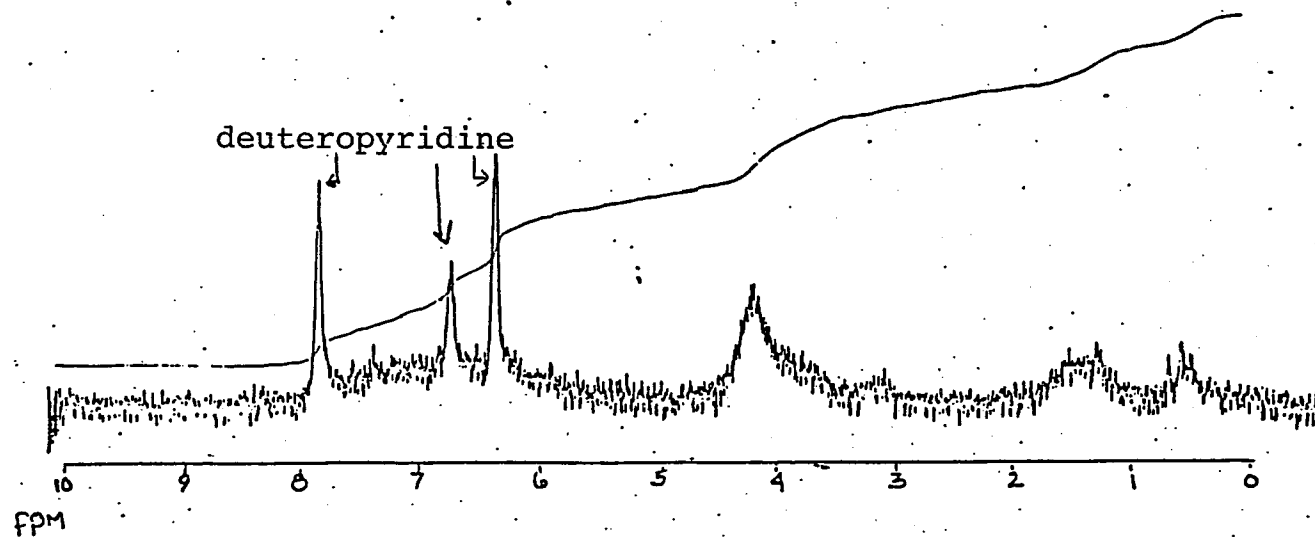


Figure 52 WKB-77 Fraction VII

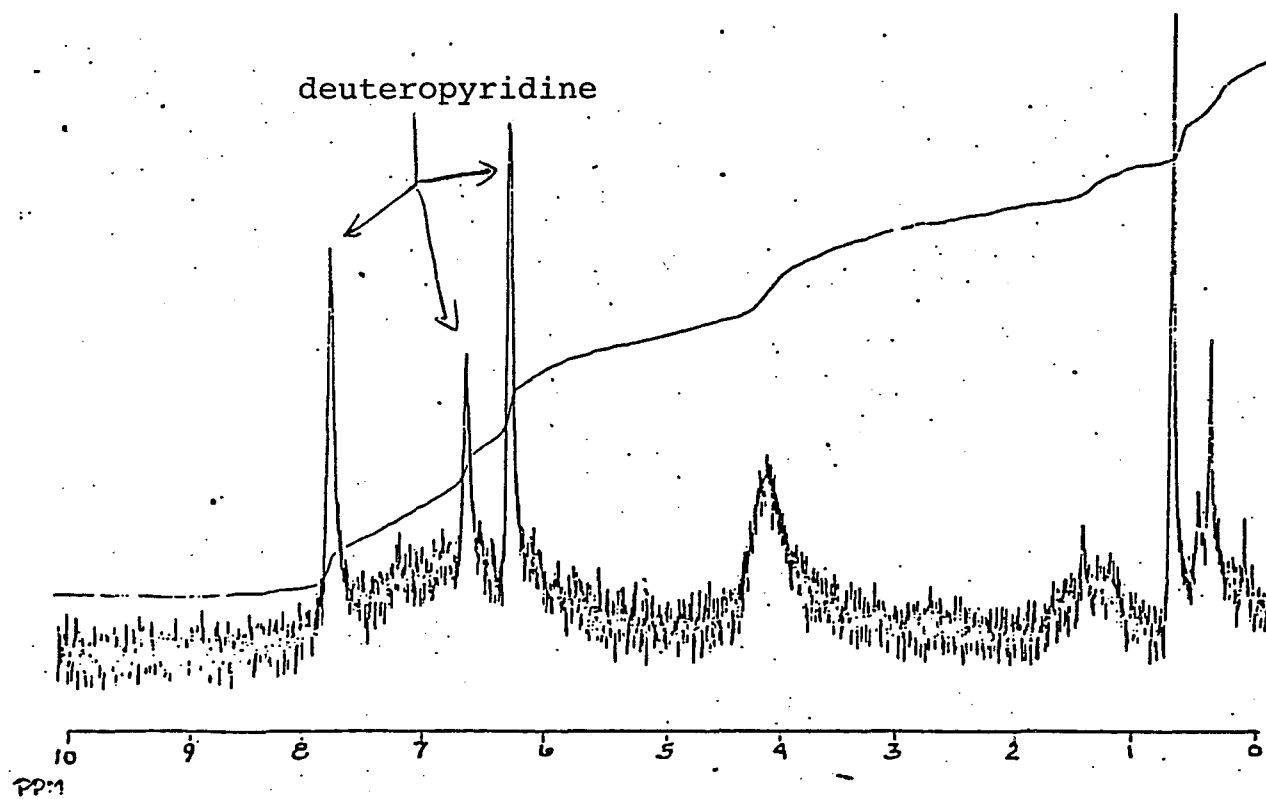


Figure 53 WKB-77 Fraction VIII

Table 17 Summary of H-NMR Results

<u>Fraction</u>	<u>Hydrogen Run</u>		<u>Steam/He Run</u>	
	<u>Percent of Aromatic Hydrogen</u>	<u>Atomic H/C</u>	<u>Percent of Aromatic Hydro</u>	<u>Atomic H/C</u>
Total Liquid	83.3	.77	89.5	.68
I	79.3	.77	75.0	.66
II	83.9	.65	83.1	.76
III	79.3	.84	92.5	.78
IV	35.9	.93	82.7	.75
V	27.5	1.02	64.1	1.31
VI	*	1.16	35.3	.82
VII	56.5	.72	42.2	1.13
VIII	30.6	*	43.8	1.39

*Insufficient

For fraction V, steam-helium run has more than twice the aromatic H content than that of hydrogen run fraction V (64.1% and 27.5% respectively). Hydrogen run fraction V has higher molar-average molecular weight than steam-helium run fraction V. The characteristic monophenols of fraction V that showed up in the 1 to 2 ppm and 6 to 7 ppm of the hydrogen run fraction spectrum appeared shifted to 2 to 3 ppm and 7 to 8 ppm in the steam-helium run fraction. The atomic hydrogen to carbon ratio of hydrogen run is higher in this fraction.

NMR of fraction VI of hydrogen run was not done due to insufficient amount of sample. The large peak in the 4 ppm region of steam-helium run fraction VI is probably due to residual methanol. However, the atomic hydrogen to carbon ratio is lower in steam-helium run, and the molecular weight is less than the corresponding fraction of hydrogen run.

The spectrum of steam-helium run fraction VII is very similar to that of hydrogen run but with extra peaks on region of 1 to 2 ppm and 3 to 4 ppm. Also, the molecular weight of the steam-helium run fraction VII is much higher than the corresponding fraction of hydrogen run, the aromatic hydrogen content is less than that of hydrogen run, and the atomic hydrogen to carbon ratio is higher than that of hydrogen run.

The spectra of fraction VIII for both coal liquids are very similar.

4.4.1 Discussion

In the present research, each modified SESC fraction was characterized by elemental analysis, hydrogen-NMR, molecular weight determination and TLC. Corresponding fractions of both hydropyrolysis and steam/helium pyrolysis liquids show almost the same structure. The following is a description of the structure of the modified SESC fractions.

The first fraction is eluted by hexane. The components of this fraction are mainly hydrocarbons and light aromatics which have low heteroatom content and low polarity. Their boiling point range is 50 to 400 C and the average molecular weight is below 190. This is the most abundant fraction in both liquids that have been studied.

The second fraction which eluted by hexane/15% benzene contains mostly aromatics with methyl or ethylene groups. Its boiling point range is about 300 to 550 C and its average molecular weight is about 200.

The third fraction eluted by chloroform includes polar aromatics with non-basic heteroatom and heterocyclics. Some heteroatom containing compounds appear in this fraction.

The boiling point range is from 300 to 600 C for this fraction. The average molecular weights are higher than that of fraction II.

The fourth fraction eluted by chloroform/10% diethyl ether contains polar aromatics with phenol and methoxy groups and also some saturated and unsaturated side chains. This fraction is even heavier, with more heteroatom content, and less aromatic than the previous fractions. No components eluted from the GC column up to 600 C, except for one peak in the hydrogen run fraction.

The fifth fraction which eluted by diethyl ether/3% ethanol has basic nitrogen heterocyclics and alcohol groups. It is less aromatic than previous fractions and its average molecular weight is higher.

The sixth fraction eluted by methanol contains basic aromatics with alcohol and methyl or $-CH_2-$ groups. Its nitrogen content is higher and its aromaticity is lower than in the other fractions. Its average molecular weight is lower than those of fractions III, IV and V. This phenomena will be discussed later.

The components of the seventh fraction are polyphenols and non-condensed aromatics. The fraction which eluted by chloroform/3% ethanol has a very high oxygen and sulfur content. But this fraction represents only a small percentage of the coal liquids in our case.

The eighth fraction which eluted by THF/3% ethanol has polyphenols with alcohol and some saturated groups, also non-condensed aromatics. It is only a small portion of the coal liquids eluted. It has the highest average molecular weight of all the fractions.

The sequence of these fractions that appears in the liquid chromatographic separation corresponds with the purpose of the method - to separate the fractions in order of increasing polarity and increasing number of functional groups per molecule. The separation followed by a more detailed characterization of the components in each fraction allows a more detailed knowledge of the structure of the liquid.

Table 12 lists the yields of major products, showing that inert gas pyrolysis (in helium) gives the lower percentage of liquids and BTX. Steam/helium pyrolysis produces more liquids, but the BTX yields remain about the same. Hydropyrolysis yields most of the liquids plus BTX of these three processes. The amount of hydrocarbon gases and BTX is larger than in the other two processes, which is an evidence of the selective conversion produced by the presence of hydrogen. While the hydropyrolysis give higher yield of gas products at the expense of liquids. In the following discussion, the differences in the nature of the liquids obtained by steam/helium pyrolysis and hydropyrolysis are discussed.

These two liquids were obtained using the same coal and under the same process conditions except one uses pure hydrogen and the other uses steam with helium as reacting gases. Hence, the differences between these two liquids are only due to the difference in reacting gases.

A comparison of the results of the elemental analysis given in Table 15 shows evidence of reactions involving hydrogen in the hydrogen pyrolysis run. The hydrogen content of the hydrogen run liquid is higher, probably due to thermal hydrogenation reactions, and the nitrogen content is lower, evidence of hydrogenolysis and heteroatom removal reactions. In consequence, the atomic hydrogen to carbon ratio is larger in the hydrogen run liquid.

There is large difference between the fractions IV and V in the aromatic hydrogen content. The hydrogen run fraction IV and V are more aliphatic in nature than the steam/helium run. The spectra of the hydrogen run of fractions VII and VIII are very similar to those of the steam/helium run.

From the atomic balance, the contents of oxygen and sulfur of the hydrogen run liquids were much smaller than the corresponding contents in the steam/helium run. This may be due to the thermal hydrogenation and heteroatom-removal reactions.

From the molecular size distribution study (Table 16), the molecular weight of the hydrogen run liquid is lower, which may be a consequence of thermal hydrocracking and free radical capping, breaking the liquid molecule down to smaller fragments under hydrolysis. For the same reason, the percentage of aliphatic hydrogen is higher in the hydrolysis run (Table 17).

Figure 34 shows a plot of the molecular weight vs. the fraction number. Since the silica gel is mildly acidic, it absorbed most of the basic coal liquids at the beginning of the separation sequence. After the first four fractions, the active sites of silica gel were deactivated by ethanol and kept inactive for the rest of the separation process. Farcasiu (1976) found that the sixth fraction which eluted by methanol is the border line between benzene soluble compounds and benzene insoluble compounds. Therefore it is not surprising that low molecular weight basic materials were eluted with the sixth eluent. Accordingly the molecular weight was increased with fraction number until fraction V, it dropped dramatically at fraction VI, then it increased with fraction number again.

Simulated boiling point distribution using gas chromatography showed that both liquids have similar characteristics; however, steam/helium run liquid includes some higher boiling point components.

From Table 12, the yield of carbon oxides in the hydrogen run is lower which may be due to the fact that carbon oxides are mostly produced from gasification, and that steam gasified the coal more than hydrogen. At the same time from the elemental analyses (Table 15), the hydrolysis liquid fractions have lower heteroatom content than steam/helium pyrolysis liquids.

It is clear that the bulk of the liquids is in fraction I and II in the case of hydrogen run, while for steam/helium run is fraction I and V. It is possible that thermal hydrocracking splitting more coal molecules into low molecular weight portions is the reason for this behavior. Also during hydrolysis, hydrogen stripping off alkyl groups (thermal dealkylation with hydrogen) probably made the first three fractions have a higher carbon content than those of the steam/helium run.

Chapter V

CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

5.1 CONCLUSIONS

The main contribution of this work is to expand the knowledge of the nature and structure of the liquid product from coal obtained by flash hydropyrolysis.

An analytical methodology has been employed in the present work to evaluate coal liquid products completely. This methodology includes the separation of coal liquids by modified SESC, followed by the characterization of GC, SEC and NMR.

Little research on these liquids has been done or published besides the information mentioned in the introduction. This knowledge is extremely important since the success of any attempt to commercialize flash hydropyrolysis as a coal partial liquefaction process will depend in great measure on the quality and the composition of the liquids.

As expected from many other processes, different coals yield different product distributions even for the same process. Two coals that have approximately the same

percentage of carbon (which is an index of the rank of the coal) gave quite different liquid product distribution during flash hydrolysis even under the same reaction conditions. This behavior must be attributed to the different internal chemical structures of these two coals molecules. The relationship between the structures of the parent coal and its liquid product requires more study.

A comparison of steam pyrolysis liquid and hydrolysis liquid leads to the conclusion that the differences in liquid product structures obtained from the same parent coal are a result of the different chemistries of these two processes. These differences are not completely understood at present. The liquid from the hydrolysis run had larger amounts of the light fractions than that from the steam pyrolysis. Coal derived liquids from hydrolysis are comparable with those from H-Coal and Synthoil processes (table 18). The liquid products from steam-helium pyrolysis are rather different from those derived from processes performed in the presence of hydrogen.

5.2 SUGGESTIONS FOR FURTHER RESEARCH

The suggestions for further study are the following: Flash hydropyrolysis liquids have higher percentages of the first two fractions, mainly hydrocarbons and aromatics, compared with coal derived liquids from other processes. The Recycle Solvent Multiple Characterization (RSMC) technique, which can separate recycle solvent of SRC process into fractions of saturated, monoaromatic, diaromatic, polyaromatic hydrocarbons, monophenols and polyfunctional components (Whitehurst et al. 1977), may be included to separate the two hydrocarbon fractions of flash hydropyrolysis liquids and would be worth studying in the future.

A more complete study of the dependence of coal derived liquids on its parent coal is needed. This will help in optimizing the processes used for various coals. From an engineering point of view, the establishment of a data bank for the modelling of flash hydropyrolysis coal liquids is essential. Treating the coal derived liquid as being composed of fractions of liquids could be a great simplification. Coal devived liquids could be modelled as composed of 'fractions' of similar polarity, molecular weight and functionality. Properties of each fraction should be measured , analyzed and incorporated into the thermodynamic correlations necessary for design and simulation work. With these properties, a more detailed evaluation of possible schemes of flash hydropyrolysis coal

liquids processing could be achieved. Separation of coal derived liquids and the establishment of selective distribution in solvents can help in the selective liquid-liquid separation processes. Experimental data are required for calculation of the multicomponent equilibrium in binary pairs. The separation of coal derived liquids is now a standard routine in plant simulation packages such as ASPEN or FLOWTRAN.

Table 18

COMPARISON OF SESC COMPOSITION OF COAL LIQUIDS FROM
DIFFERENT SOURCES

<u>FRACTION No.</u>	<u>WEST KENTUCKY* S.R.C.</u>	<u>CITIES SERVICE F.H. LIQUID</u>		<u>H.R.I.* H-COAL</u>	<u>ERDA* SYNTHOIL</u>
		<u>H₂ Run</u>	<u>Steam/He Run</u>		
I + II	15.4	60.0	37.1	69.5	52.4
III	30.0	5.3	12.8	12.91	31.8
IV	10.2	2.3	2.2	8.12	10.0
V	10.1	0.3	31.5	2.7	1.6
VI	4.1	17.8	2.4	2.5	1.0
VII	6.4	0.2	1.4	2.14	1.1
VIII + IX	18.7	14.1**	12.6**	1.1	1.0

*DATA PUBLISHED BY D.D. WHITEHURST ET AL., 1976

** Residual calculated by material balance

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